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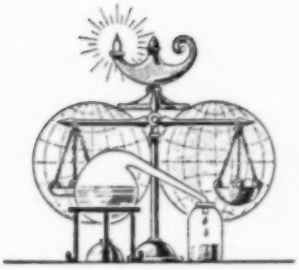

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FOREWORD

Until a few years ago there was no systematic or unified policy with regard to the publication of reports and papers prepared by the International Union of Pure and Applied Chemistry (I.U.P.A.C.) through its Commissions, Sections and Divisions. The Nomenclature rules for different branches of chemistry, drawn up and revised from time to time, after careful consideration, by the co-operative effort of experts in different countries, were satisfactorily publicized through scientific journals and societies in different member countries. On the other hand, there was often a feeling of dissatisfaction that many other important Commission reports and standardization procedures failed to receive a sufficiently wide distribution and recognition. The difficulties have increased with the growth of chemistry and as the activities of the Union have widened in range. The view has often been expressed that it would be more satisfactory if all the scientific work of the Union could be collected for reference in one publication.

At the Paris meeting of 1957, a Publications Committee was set up to examine more efficient ways of publishing and disseminating the Union's work. Subsequently a commercial publisher was appointed and during the past three years a number of reports have been issued with encouraging success. At Munich in 1959 the Council of I.U.P.A.C. took a further step to bring all the publications together in a journal of its own and the Publications Committee has therefore been reinforced by the formation of an Editorial Advisory Board, members of which are listed on the inside front cover. In addition to I.U.P.A.C. publications, the new journal will also carry, when appropriate, reports of meetings and symposia held under the aegis of the International Council of Scientific Unions (I.C.S.U.).

The policy of including in one journal a number of reports dealing with very different aspects of chemistry may at first sight be open to question. However, any such objection is fully answered by the arrangement which has been made for separate issues and the sale of reprints, in pamphlet or book form, as appropriate, of each particular article, report or symposium. If the present plan proves successful it should lead to a wider appreciation of the Union's activities and of the work carried out by authors of reports prepared under its auspices. In addition other advantages already set out in the Union's bulletins should accrue both to the Union and to individual scientists. The Union will retain the copyright of all material included in the journal but, as in the recent past, arrangements may be made with the publisher for the reprinting of certain articles elsewhere if this is requested, often without a royalty being charged to the national society or organization concerned. A document setting out other details of policy was recently issued to all officers of Sections, Divisions and

Commissions, and is available for all who may be concerned in the future. A brief account of the organization and functions of I.U.P.A.C. is given in the pages following this foreword.

Any comments or criticisms which will help the Editorial Advisory Board in their effort to achieve the aims of the new journal will be welcomed.

H. W. THOMPSON

Chairman, Editorial Advisory Board

Oxford, February, 1960

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THE ORGANIZATION AND FUNCTIONS OF THE INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

(I.U.P.A.C.)

W. A. Noyes, Jr. and H. W. Thompson

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CONSTITUTION

The International Union of Pure and Applied Chemistry is a voluntary organization. Its chief purpose is to establish and promote co-operation between the Chemical Societies of the member countries, and to co-ordinate their scientific and technical activities. The governing body of the Union, its Council, is composed of delegates appointed by national agencies concerned with fundamental and applied chemistry in the participating countries. These agencies, which represent the chemical interests of the country concerned (e.g., Comité National de la Chimie, under the aegis of the Académie des Sciences, France; British National Committee for Chemistry of the Royal Society, England; Division of Chemistry and Chemical Technology of the National Research Council, U.S.A.; The Academy of Sciences in Moscow, U.S.S.R.) are the adhering bodies to I.U.P.A.C. At present there are 37 national adhering bodies (see p. 9).

Internationally, the importance of chemistry has long been recognized and during the fifty years preceding the First World War there were many attempts at collaborative action. The Union, as we know it today, originated in London in November 1918, through the joint action of Sir William Pope, then President of the Society of Chemical Industry, and Paul Kestner, at that time President of the Société de Chimie Industrielle. It was formally constituted at a meeting in Rome in June 1920.

FUNCTION

The Union is essentially concerned with those aspects of chemistry, both pure and applied, about which international agreement or uniform practice is desirable. Examples are nomenclature, atomic weights, symbols and terminology, physicochemical constants, and certain methods of analysis and assay. At the biennial conferences of the Union reports on such subjects are presented for discussion by the appropriate Commissions dealing with them and, after approval, are published.

Thus, the Union, through its Commissions, offers an international forum where outstanding specialists in many fields of interest can meet to exchange opinions and experiences with the object of reaching agreements which will promote the progress of chemistry throughout the world. The adoption of these agreements or recommendations is not mandatory for the adhering countries and remains voluntary. Nevertheless, the expert

judgment which goes into them, and the care taken to consider all points of view has usually led to their general acceptance.

The Union also sponsors international congresses and symposia organized by its Sections or Commissions in their respective fields of interest. A general international Congress was held in New York City in 1951, in conjunction with the Diamond Jubilee meetings of the American Chemical Society. In Sweden in 1953, there were held a Congress of Physical Chemistry, and Symposia on Macromolecules and on the Chemistry of Wood and its Constituents. The XVIIIth International Conference and the XIVth International Congress of Pure and Applied Chemistry (Organic Chemistry) took place in Zurich in 1955. The XVth International Congress dealing with Analytical Chemistry was held in 1956 in Lisbon. The XIXth International Conference and the XVIth International Congress were held in Paris in 1957 following the Centenary Celebration of the Société chimique de France. The Congress covered the subjects of Physical, Inorganic and Organic Chemistry. The XXth International Conference and XVIIth International Congress of Pure and Applied Chemistry were held in Munich between August 25 and September 6 1959. The XVIIth International Congress dealt mainly with Inorganic Chemistry, but also with Biological Chemistry. The XVIIIth International Congress will be held in Montreal, at the invitation of the Canadian National Research Council in 1961.

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MECHANISM

The structure of the Union is shown on p. 10. The executive agency of the Council is the Bureau, composed of the President, two past Presidents, the Secretary-General, the Treasurer, the Presidents of the six Sections, three Vice-Presidents (elected by the Council) and eight Members elected by the Council. Thus the total membership of the Bureau is now 22. The Executive Committee of seven members, consisting of the President, Secretary-General, Treasurer and four members of the Bureau acts between meetings of the Bureau.

At the XXth Conference the following Executive Committee was appointed:

W. A. Noyes, Jr., President of the Union, The University of Rochester, Rochester 20, New York (U.S.A.)
Sir Charles Dodds, Treasurer, Courtauld Institute of Biochemistry, The Middlesex Hospital Medical School, London, W.1 (U.K.)
B. A. Kasanski, Section de Chimie de l'Académie des Sciences, Moscow (U.S.S.R.)
W. Klemm, Anorganisch-chemisches Institut der Universität, Hindenburgplatz 55, Münster, Westf. (Federal German Republic)
M. Letort, Director-General, Cerchar, 35 rue St-Dominique, Paris 7-e (France)
R. Morf, Secretary-General, c/o F. Hoffmann-La Roche & Co. Ltd., Basle 2 (Switzerland)
Sir Alexander Todd, Chemical Laboratory of the University, Lensfield Road, Cambridge (U.K.)

The Union is divided into six Sections, five of which are concerned with the five principal branches of fundamental chemistry, and the sixth with the general field of applied chemistry. The Sections are practically autonomous, except in respect of financial matters. They elect their own officers and can, subject to the approval of the Bureau, form or dissolve Commissions. A Section may organize itself by Divisions, each of which may sponsor several Commissions. The only Section which thus far has made use of the divisional organization is that of Applied Chemistry. The titles of the Divisions (see p. 10) indicate the reason for this type of organization in the very broad field of applied chemistry.

The ultimate working units of the Union are the Commissions, and in a number of cases Sub-Commissions. Each Commission is associated with, and responsible to, a Section of the Union. Much of the work of the Commissions is conducted by correspondence, but it is obviously necessary, for effective collaboration, for Commissions to convene at intervals, preferably at least once in two years. To promote such meetings the Union grants a partial subsidy of travel expenses so far as its meagre funds allow.

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During the past few years I.U.P.A.C. activity was concentrated on the establishment of Nomenclature Rules and the compilation of data on atomic weights.

The Physical Chemistry Section has published a *Manual of Physico-Chemical Symbols and Terminology* (in English and French) by the appropriate Commission.

The Inorganic Chemistry Section has elaborated *Definitive Rules for Nomenclature of Inorganic Chemistry*.

The Commission on Atomic Weights brought up to date the *Table of Atomic Weights* of 1957, and a *Table of the Radio-active Elements* in 1957.

The new scale for atomic weights and nuclear masses will be established in 1961.

The Organic Chemistry and Biological Chemistry Sections have issued the *Definitive Rules for Nomenclature of Organic Chemistry*.

With the aim of better dissemination of scientific knowledge a new international journal, *Pure and Applied Chemistry*, has now been created by the Union.

FINANCIAL SUPPORT

All the officers of I.U.P.A.C. carry out their duties on an honorary basis and without cost to the Union. Administrative expenses are therefore small. The Union's funds are derived from two sources, namely national contributions, and grants-in-aid from U.N.E.S.C.O., with which the Union is affiliated through the International Council of Scientific Unions (I.C.S.U.). National contributions are in three categories. At the 1953 Conference in Stockholm the national contributions were fixed as follows: member countries in Category A, $1,300; member countries in Category B, $800; member countries in Category C, $450. A revision of these contributions is now under discussion. The expanding programme of U.N.E.S.C.O. has meant that successive budgets approved by General

Conferences of U.N.E.S.C.O. have scarcely kept up with inflation, and grants to the International Council of Scientific Unions are actually smaller than they were ten years ago. Since there are now 13 member Unions (two new ones were admitted in 1955) and an increasing amount of activity directly under the aegis of I.C.S.U., it is evident that contributions from U.N.E.S.C.O. (through I.C.S.U.) to the Union of Pure and Applied Chemistry do not cover more than a small fraction of total costs. Added income must be found if the Union and its Sections and Commissions are to do more effective work.

I.U.P.A.C.—NATIONAL ADHERING BODIES

ARGENTINA Asociación Química Argentina, Hipolito Yrigoyen 679, Buenos Aires
AUSTRALIA Australian Academy of Science, Gordon Street, Canberra City, A.C.T.
AUSTRIA Verein Österreichischer Chemiker, Eschenbachgasse 9, III. Stock, Wien 1
BELGIUM Comité National Belge de Chimie, Prof. J. GILLIS, 22, rue J. Plateau, Gand
BRAZIL Associação Brasileira de Química, Caixa Postal 550, Rio de Janeiro
BULGARIA Académie des Sciences de Bulgarie, Sofia
CANADA National Research Council, Division of Chemistry, Ottawa
CHINA (TAIWAN) Chinese Chemical Society, P.O.B. 609, Taipei Taiwan
COLOMBIA Ministerio de Minas y Petroleos, Laboratorio Químico Nacional, Apartado 2577, Bogotá
CZECHOSLOVAKIA Chemical Society of Czechoslovakia, Dr JAN JELINEK, Gregova 12, Prague 12
DENMARK Danske Kemiske Foreningers Faellesraad for internationalts Samarbejde, 83, Sölvgade, Copenhagen K
FINLAND Suomen Kemistien Valtuuskunte, P.O.B. 58, Helsinki
FRANCE Comité National de la Chimie, 28, rue St-Dominique, Paris-7e
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ITALY Consiglio Nazionale delle Ricerche, Comitato per la Chimica, Piazzale delle Scienze 7, Rome
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SWITZERLAND Comité suisse de la Chimie, Ecole de Chimie, 22, bd des Philosophes, Genève
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TURKEY Türkije Kimya Cemiyeti Merkezi, Istiklâl Caddesi, Imam Sodak nº 22, Kat. I-Beyoglu, Istanbul 829
UNITED ARAB REPUBLIC National Research Council, Ministry of Education Sh. al-Tahrir, Dokki, Cairo
UNITED KINGDOM British National Committee for Chemistry, Burlington House, Piccadilly, London W.1
UNITED STATES National Research Council, Division of Chemistry and Chemical Technology, 2101 Constitution Avenue, Washington 25 D.C.
U.S.S.R. Academy of Sciences, B. Kaluszkaya 14, Moscow
VENEZUELA Sociedad Venezolana de Química, Apartado 3895, Caracas
YUGOSLAVIA Union des Soc. chim. de la R.P.F.Y., Dr P. Tutundžić, boîte postale 494, Belgrade

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Appendix 2

THE STRUCTURE OF THE UNION

THE COUNCIL

THE BUREAU

THE EXECUTIVE COMMITTEE

THE EDITORIAL BOARD

Sections	Commissions	Subcommissions
Analytical Chemistry	Analytical Reactions	
	Microchemical Techniques	
	Terminology and Expression of Analytical Results	
	Optical Data	
	Electrochemical Data	
	Equilibrium Data	
Applied Chemistry Divisions:	Food	Subdivisions: Vitamin Assay; Trace Elements; Additives to Food
	Water, Sewage and Industrial Wastes	
	Oils and Fats	
	Pulp, Paper and Board	
	Plastics and High Polymers	
	Pesticides	
	Organic Coatings	
	Fermentation	
	Toxicology and Industrial Hygiene	
	Ad Hoc Committee on Chemical Engineering	
	Ad Hoc Committee on Surface Activants	
Biological Chemistry	Nomenclature of Biological Chemistry	Nomenclature of Phosphatides; Nomenclature of Pectin-Hydrolysing Enzymes
	Protein Standards	Standardization of Enzyme Analysis
	Clinical Chemistry	
Inorganic Chemistry	Atomic Weights	
	Nomenclature of Inorganic Chemistry	
	High Temperatures and Refractories	Gases; Condensed States
	Geochemistry	
Organic Chemistry	Nomenclature of Organic Chemistry	
	Codification, Ciphering and Punched-card Techniques	
Physical Chemistry	Physico-Chemical Symbols and Terminology	
	Chemical Thermodynamics	Experimental Thermochemistry; Experimental Thermodynamics
	Electrochemistry	
	Affiliated Commission: International Committee for Electrochemical Thermodynamics and Kinetics	
	Macromolecules	Standard Samples; Nomenclature; Publications
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	Molecular Structure and Spectroscopy	
	Applied Radioactivity (Joint)	

INTERNATIONAL ATOMIC ENERGY AGENCY

JOINT COMMISSION ON APPLIED RADIOACTIVITY
(I.C.S.U.)

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Proceedings of the

RADIOACTIVATION ANALYSIS SYMPOSIUM

Vienna, Austria

June 1959

INTRODUCTION

Radioactivation Analysis is a relatively new technique. During the last years it has been perfected. All sciences, but especially biology, biochemistry, geology and chemistry have much to gain by its use, which enhances the accuracy of analytical methods, and, in many cases, with its help much smaller amounts can be determined than had been possible hitherto by using conventional methods.

It has been the aim of the Joint Commission on Applied Radioactivity to make this new technique, so widely applicable, known to all scientists who may benefit by its use and at the same time exchange the latest knowledge in the field. For this reason the Joint Commission on Applied Radioactivity had for some time planned such a Symposium but it was not until the International Atomic Energy Agency was created and able to co-sponsor such a meeting, that the necessary funds were available to hold such an important Symposium.

The full discussion of the Symposium is incorporated in these proceedings, which should fulfil the Committee's aim of giving the widest possible dissemination of the latest developments. This application of atomic energy is relatively cheap and so nothing should stand in the way of using it much more widely than in the past.

It is with this aim that I recommend this publication to the attention of my colleagues.

HENRY SELIGMAN
President
Joint Commission on Applied Radioactivity (I.C.S.U.)

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SCIENTIFIC PROGRAMME

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RADIOACTIVATION ANALYSIS IN A NUCLEAR REACTOR

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L'analyse par radioactivation est une méthode très efficace qui permet de déterminer les quantités de nombreux éléments présents à l'état de traces sans que, généralement, le gros de l'échantillon perturbe gravement les opérations. La sensibilité, qui est grande pour de nombreux éléments, dépend de ce que, avec les flux de neutrons et les détecteurs dont on dispose, il est possible d'induire dans un microgramme, et même dans une quantité moindre d'un grand nombre d'éléments, des quantités de radioisotopes faciles à déterminer. Les facteurs qui influent sur la sensibilité, dans l'équation fondamentale de l'activation sont: le flux de neutrons, la section efficace d'activation des neutrons lents et, dans une moindre mesure, la période du radioisotope produit. Il n'est cependant pas possible de faire des analyses exactes en recourant à l'equation fondamentale pour le calcul des résultats, parce qu'on ne connait pas avec une précision suffisante la valeur numérique des différents facteurs. Pour surmonter cette difficulté, un poids connu de l'élément recherché (désigné ci-après par T, pour abréger) est irradié avec l'échantillon, ce qui permet d'établir un rapport entre le taux de désintégration et le poids de T, et d'appliquer ce rapport au taux de désintégration de T constaté dans l'échantillon.

Après activation, on peut recourir à deux méthodes d'analyse différentes. Si les principaux éléments composant l'échantillon possèdent des radioisotopes à période courte (par exemple, Al ou Si, *etc.*), on peut les laisser se désintégrer de manière à pouvoir examiner les traces des radioisotopes à longue période que présentent les impuretés, sans perturbations dues à des quantités importantes d'autres isotopes. En pareil cas, on pourra, à l'aide d'un spectromètre à scintillation, mesurer une émission éventuelle de rayons gamma, sans avoir à détruire l'échantillon. Toutefois, de tels cas sont exceptionnels; le plus souvent, le traitement chimique s'impose. Les quantités d'oligo-éléments sont trop faibles pour permettre une simple manipulation chimique; c'est pourquoi on ajoute, après dissolution de l'échantillon, un poids connu de T inactif (généralement de 10 à 50 mg) comme entraîneur. Il faut que l'entraîneur et la trace soient ramenés à un même état chimique (s'il existe plusieurs possibilités); on sépare et on épure T de manière à le rendre chimiquement et radiochimiquement pur. Il n'est pas nécessaire que le processus de séparation soit quantitatif, puisqu'on peut déterminer le rendement chimique. Enfin, on détermine la radioactivité de T par un moyen approprié et on la compare à celle d'un poids connu du produit type.

On peut apercevoir, dans cette méthode, plusieurs sources d'erreurs. Une des plus importantes est celle qui résulte de l'absorption des neutrons. Si l'échantillon ou l'étalon contient des quantités appréciables d'un élément à grande section efficace de capture de neutrons, le flux de neutrons au centre peut différer sensiblement de ce qu'il est à la surface, de sorte que les conditions moyennes auxquelles l'échantillon et l'étalon sont exposés risquent de ne pas être les mêmes, ce qui entraine des erreurs. D'autre part, la plupart des irradiations se produisent dans des réacteurs où il existe un flux appréciable de neutrons rapides (énergie supérieure à 1 MeV). Ceux-ci peuvent entrer en réaction avec les principaux éléments de l'échantillon (surtout par des réactions (n,p) et (n,α)) et constituer, dans certains cas, le même produit radioactif que celui qui résulte de l'action des neutrons lents sur une trace d'impureté stable Si donc l'élément recherché a un nombre atomique qui est inférieur de 1 ou 2 à celui de l'un quelconque des principaux constituants, des erreurs peuvent se produire du fait qu'il y aura une apparente impureté à l'état de trace, provoquée par les neutrons rapides.

En plus de sa haute sensibilité, la méthode par radioactivation présente un certain nombre d'autres avantages, dont un des plus importants est qu'il n'est pas nécessaire de faire de correction d'après témoin. L'auteur signale d'autres avantages et inconvénients.

GENERAL PRINCIPLES

As is well known, the equation relating the radioactivity induced in an isotopic species subjected to a constant flux of neutrons (f) with the number of atoms of that species in the target is

$$A_X = f\sigma_a N_X(1 - e^{-\lambda t}) \qquad (1)$$

where N_X is the number of target atoms of type X with an activation cross-section for the bombarding particles of σ_a. A_X the disintegration rate of the radioisotope produced from X as a result of the bombardment, λ its disintegration constant and t the time of bombardment. As N_X is related to mass by Avogadro's number and the atomic weight, the disintegration rate may be related to mass, and hence the possibility of analytical use. If some typical figures are substituted in the equation above, one of the great advantages of radioactivation as a method of analysis, its high sensitivity, becomes obvious. Let us take the case of sodium irradiated in a reactor with a flux of thermal neutrons of 10^{12} cm^{-2} sec^{-1}, a value that is readily available today. The activation cross-section is $0{\cdot}54 \times 10^{-24}$ cm^{-2}, and we will assume that the detector of radiation has an overall efficiency of 10 per cent. Assuming 1 count per second detected to be significant, then $10 = 10^{12} \times 0{\cdot}54 \times 10^{-24} \times N(1 - e^{-\lambda t})$. The radioisotope of sodium produced, ^{24}Na, has a half-life of 15 h so that for an irradiation time of 3 days, the term $(1 - e^{-\lambda t})$ or $(1 - e^{-0{\cdot}693\, t/t_{\frac{1}{2}}})$ equals $(1 - e^{-3{\cdot}3})$ or $(1 - 0{\cdot}036)$ which we can call 1. Therefore $N = 10^{13}/0{\cdot}54$ or $1{\cdot}85 \times 10^{13}$ atoms or 7×10^{-10} g of sodium.

The equation shows that the sensitivity is directly proportional to both σ_a and the flux. Many isotopes have activation cross-sections appreciably higher than that of sodium and the sensitivity is correspondingly greater. In some cases, however, the cross-section is much lower and sensitivity may be reduced to that of earlier methods, although with a flux value of 10^{12} neutrons cm^{-2} sec^{-1}, this is not often the case. Even in such cases, improvement can be obtained by increasing the neutron flux, and values of 10^{13} and even 10^{14} can be obtained, although not readily.

The half-life of the radioisotope produced enters into the sensitivity in two ways. Firstly, it is included in the term $(1 - e^{-\lambda t})$. If the half-life is short compared with the irradiation time, this factor tends to 1, but the length of irradiation has practical limits (irradiations longer than 1 month become inconvenient), so that if the half-life is long compared with the irradiation time, $(1 - e^{-\lambda t})$ is appreciably less than 1. For example, it has the value of only 0·01 for ^{60}Co ($t_{\frac{1}{2}} = 5{\cdot}2$ years) for a month's bombardment. After irradiation, the manipulations required before making a measurement of the radioactivity must not take so long that an appreciable fraction of the nuclide decays. Thus if a time corresponding to three half-lives is required, a loss of sensitivity by a factor of eight occurs. Since some procedures are quite time-consuming this can be a serious limitation for radioisotopes with half-lives of about 30 min or less, but in certain cases where manipulation is a minimum, elements with isotopes of half-lives less than 1 min have been analysed.

EXPERIMENTAL METHODS

Whilst, theoretically, the amount of an element can be determined from equation (1) above, the experimental uncertainties in the values are so great that a much simpler and more accurate comparative method is always used. The sample is irradiated with a " standard ", a known weight of the element sought. The two, usually in the same container, are thus subjected to the same irradiation conditions. From the disintegration rate per unit weight of element from the standard, the determined disintegration rate of the element sought from the sample may be converted to weight by simple proportions.

Treatment of the sample before irradiation is relatively simple, but great care, of course, must be taken to avoid accidental contamination, as with any method of trace analysis. Samples are often sealed in polythene containers for short irradiations (up to a few days) or in silica for longer times.

Non-destructive analysis

After irradiation, all elements of the sample are radioactive. The half-lives of the various activities produced will, of course, depend on the composition, but in certain cases the half-life of the main bulk of the sample is much shorter than those of some of the trace impurities. After a suitable decay period, therefore, only the trace elements remain active. This happens for instance in the trace analysis of super-pure aluminium ($t_{\frac{1}{2}} = 2{\cdot}3$ min) and silicon ($t_{\frac{1}{2}} = 2{\cdot}6$ h) which are industrially important. Advantage is taken of this fact to carry out a rapid, non-destructive analysis of the samples, since the trace impurities can now be measured directly[1–4]. Some means of discriminating between the various activities must be available since several are usually involved. For β-particle emitters, this is possible by half-life and β-absorption curve resolution, but this tends to be cumbersome and time consuming. The most suitable technique is γ-ray analysis using the γ-ray scintillation spectrometer. With this instrument, the characteristic γ-energies (and their abundances) of a given nuclide can be recognized and quantitative estimates made of the amount of radiation detected either from the photoelectric peak height or its area on the pen-recorder tracing, using the standard to normalize the determined quantity to weight. However, since a γ-ray energy is not a unique identification of a nuclide, some further assurances of identity may be necessary. These can be provided by the detection of the other γ-rays known to be emitted by the nuclide, if its decay scheme is complex, and from half-life determinations.

When using the single-channel pulse analyser, the sensitivity of detection using the γ-scintillation spectrometer is less by a factor of at least 20 than that of methods involving determination of β-particles. Some gain in sensitivity is obtained by using a multichannel pulse analyser, particularly when applied to short-lived isotopes as these decay appreciably during the time of a scan by the single-channel instrument. The attractions of this approach to activation analysis are so obvious that further improvements both in reliability and price of instruments are to be expected.

In an attempt to overcome some of the difficulties mentioned above, Putman and Taylor[5] devised a method whereby the greater activity on the base material can be eliminated to reveal the γ-trace of the impurity. Two sodium iodide scintillation counters are used and their outputs are balanced and subtracted electronically from each other, so that when identical radioactive samples are viewed by both, the net output is nil. If now two samples, one differing from the other only by the presence of a trace impurity, are irradiated together and the γ-activity examined as above, the resultant record is that of the trace impurity. This was shown to be quite practical in an investigation of the amount of selenium retained by a glass, using the contaminated glass as one sample and the untreated glass as the other. Clearly, this method is somewhat restricted in application, but may be of use in special cases and is perhaps worthy of further investigation.

Method involving chemical separation

The majority of samples cannot be examined by γ-ray spectroscopy alone because of the residual radioactivity from the main bulk of the sample. In this case, a chemical separation is necessary. After irradiation, the sample is dissolved in a suitable medium and a small, known quantity (usually 10–50 mg) of the trace element in question is added to the solution to act as a " carrier " so that chemical manipulations, such as precipitation, not possible with the original 10^{-6} g or less, can be performed.

Steps must now be taken to ensure that the carrier and trace are brought to the same chemical state, if several exist, for obvious reasons. Then some predetermined chemical separation is performed which will yield the element sought in a chemically and radiochemically pure state. The separation need not be quantitative as correction for chemical losses can easily be made from the initial and final weight of carrier. The estimation of the chemical yield is usually made gravimetrically, although other means are not excluded. The β- and γ-activities of the sample are now determined by suitable means and the radiochemical purity of the specimen can be verified by half-life, β- and γ-energy determinations. If the activity of the standard is determined with the same apparatus, the many possible sources of error due to scattering of radiation are eliminated. A possible exception to this is the correction for self-absorption in the precipitate. This too can be avoided by ensuring that the sample and standard precipitate have the same weight, but care is needed if the β-energy is very low (*e.g.*, ^{35}S, ^{14}C), because small differences in weight may have appreciable effects. The sensitivity by β-particle determination for elements which can be analysed by radioactivation has been compiled and published by Smales and Jenkins[6].

In certain cases where a chemical procedure is required it is possible to shorten the analysis by using a simple separation which removes the main radioactive component from the trace activity. The determination of the amount of trace activity is now carried out by γ-spectroscopy where resolution of the γ-components of the mixture acts as a further stage of separation. This can appreciably shorten the analysis as chemical procedures are usually multistage processes. We have found this very useful for biological samples where sodium (as sodium-24) is nearly always present.

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SOURCES OF ERROR

As in all methods of analysis, certain sources of error, other than faults of commission, must be recognized.

Secondary nuclear effects

In the reactor, radioactivation analysis depends on the fact that an element, T, captures a neutron to form the nuclide (T + 1), from the disintegration rate of which the mass of T can be determined. If (T + 1) can be formed by means other than this reaction, errors will be introduced. Production of (T + 1) is possible in several ways. Firstly, if (T + 1) is a fission product of uranium or other fissile material, traces of these elements will introduce (T + 1) in an amount unrelated to the mass of T present. Secondly, some isotopes capture slow neutrons to yield a radioactive isotope which decays not to a stable species, but to another radioactive one. If this should be (T + 1), analysis is impossible, and even if it is another isotope of T, the amount may be sufficient to interfere with the measurement of the small amount of (T + 1). Thirdly, all reactors have a flux of fast neutrons which are sufficiently energetic to cause nuclear reactions involving the emission of a charged particle, so that a change of element is involved. Thus, in the B.E.P.O. reactor at Harwell, copper-64 is produced by the (n,p) reaction on pure zinc, in an amount equivalent to that which would be produced from 700 parts per million of natural copper in the zinc[7]. Similarly, (n,α) reactions occur, though usually with lower yield than for (n,p) reactions. For instance, the ^{27}Al (n,α) ^{24}Na reaction occurs to an extent equivalent to 80 parts/million of natural sodium[8]. On the other hand, there was no interference from the ^{109}Ag (n,p) ^{109}Pd reaction in the analysis of palladium in silver[1]. In determining trace elements which are one or two atomic numbers less that any major component of the sample (*i.e.*, equivalent to the (n,p) and (n,α) reactions respectively), the possibility of an error from this cause must be considered although it may be negligible. Since the ratio of fast to slow neutrons varies with the type of reactor and with the irradiation position in the reactor, each case must be treated on its own merits. Some information does exist about the cross-sections of such reactions with pile neutrons but it is by no means complete or consistent[7, 9].

A less common effect is the production of the trace impurity by successive neutron capture. This was noted some time ago by Smales *et al.*[10] in the analysis of arsenic in germanium transistor material. Natural arsenic (^{75}As) is determined by the production of ^{76}As, but at the same time stable germanium-74 produces ^{75}Ge which decays by β-particle emission to form ^{75}As which in turn is another route to the formation of the required ^{76}As. The order of magnitude of these effects is an error of +0·08 parts/million of arsenic for a 75 h irradiation at 2×10^{12} neutrons cm^{-2} sec^{-1} but only +0·0001 parts/million for 10 h at 2×10^{11} neutrons cm^{-2} sec^{-1}. However, as reactors of high flux (10^{13} neutrons cm^{-2} sec^{-1} and greater) are becoming available, greater attention must be directed to this possibility, as the effects vary as the square of the flux.

Another factor which may be appreciable, but probably only occasionally, even in high flux reactors, is the destruction of the required product of

neutron capture by a further event. Thus natural gold-197 produces gold-198, which has a half-life of 2·7 days, but a slow neutron capture cross-section of 19,000 barns, and gold-199, which is also radioactive, can be detected in appreciable quantities in many gold-198 preparations. This effect is also dependent on the square of the neutron flux, the time of irradiation and the capture cross-section of the radioactive isotope, which is known in only a few cases.

The effects noted above can usually be recognized and in some cases eliminated. If the element sought is known to be a fission product, the presence of the other fission products can be used to indicate the presence of uranium, if this itself is not recognized. Tables of radioisotopes will indicate whether isotopes of the trace element can be formed from components of the sample, provided the composition is known. This will also indicate whether formation by (n,p) or (n,α) reactions is a possibility. Should this be the case, irradiation in a purely slow neutron flux is indicated, although this means a severe loss of sensitivity, because pure slow neutron fluxes comparable with the heteroenergetic fluxes within the core of a reactor are not available. It is also possible to correct for such effects by irradiation of the samples and standards in neutron fluxes with different ratios of fast to slow neutrons, and solving two simultaneous equations. This inevitably introduces a greater error than normal, since two determinations are involved, and will fail experimentally if the amount of T + 1 formed from T is much smaller than that from other sources. The remaining two effects, depending as they do on the square of the flux, will be recognized from results obtained from irradiations at different fluxes.

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Neutron shielding effects

A basic condition of the radioactivation method is that the sample and standard are irradiated under identical conditions. If, however, the sample has components of high neutron capture cross-section, the neutron flux at the centre of the sample will be significantly less than that at the surface, and the average flux to which the sample is subjected is different from that of the non-absorbing standard. This difficulty may be minimized by using as small a sample as possible, but is best overcome by constructing a correction curve from samples of known composition. In the worst case another analytical technique must be sought. If the standard has a high cross-section, the difficulty is overcome by using a weight so small that neutron self-shielding is insignificant. This is most easily done by irradiating a very dilute solution of the standard.

This we prefer to dilution with solid as pure water is more readily available than a pure solid. Various formulae have been derived to calculate the neutron self-shielding cross-sections[1, 11], but these are dependent on the shape of the sample and are usually based on the thermal neutron absorption cross-section. Pile neutrons are, however, not truly thermal in energy and many isotopes have pronounced resonance absorption effects just above the thermal energy region. We find it best to use the formula only as a guide to the order of magnitude of the effect and to determine experimentally the maximum concentration below which such effects can be neglected. Plumb and Lewis[12] have also pointed out that the differential

absorption of resonance neutrons can cause differences in the proportions of radionuclides from different isotopes of the same element in samples of different sizes.

FAST PARTICLE ACTIVATION ANALYSIS IN REACTORS

The majority of radioactivation analyses in the pile depend on the (slow neutron, gamma) reaction. Occasionally it is possible to use other reactions which occur in the pile. Thus, although sulphur can be analysed by the production of sulphur-35, the cross-section for the reaction is low, the half-life of ^{35}S is relatively long and the β-particles are of low energy ($E_{max} = 0{\cdot}167$ MeV). There is also interference from the chlorine (n,p) sulphur-35 reaction. On the other hand, the yield of phosphorus-32 by the ^{32}S (n,p) ^{32}P reaction is relatively high, and in fact the sensitivity is greater for the latter method. Experimentally, there is the added advantage that the energetic β-particles of ^{32}P are measured (1·7 MeV). However, in this case, ^{32}P can also be produced by ^{31}P (n,γ) reaction so that the phosphorus content of the sample must be known. Alternatively, this can be determined by irradiation of samples and standards in two positions of differing flux ratios of fast to slow neutrons and solving two simultaneous equations. Another example is the analysis of nickel by the ^{58}Ni (n,p) ^{58}Co reaction, which has a relatively high cross-section, and in this case, we have the advantage that cobalt-58 cannot be produced by neutron capture in natural cobalt contamination.

Another interesting example was demonstrated by Osmond and Smales[13]. Lithium-6 on irradiation with slow neutrons disintegrates to produce energetic alpha and tritium particles by the reaction ^{6}Li (n, ^{3}H) ^{4}He. The triton has an energy of 1·78 MeV, sufficient to cause further nuclear reactions. In this case, it was used to estimate oxygen by the amount of fluorine-18 ($t_{\frac{1}{2}} = 112$ min) produced by the ^{16}O (^{3}H, n) ^{18}F reaction. The method consists of irradiating an intimate mixture of a suitable lithium compound (LiF was used) with the finely divided sample, in this case beryllium metal containing a trace of oxide. A limiting sensitivity of 5×10^{-7} g of oxygen has been given, but several experimental difficulties exist. Thus the lithium compound must be free of oxygen to these limits, and the effects of grain size of the sample must be controllable, as the penetrating power of the recoil triton in matter is very small. In principle, the same reaction could be used to estimate lithium, although the direct estimation by the amount of tritium produced is more sensitive[6].

The cyclotron and betatron have also been used as the activating source for radioactivation analysis. The experimental difficulties are much greater than with a reactor and these problems will not be discussed here.

ADVANTAGES OF THE METHOD

Although some emphasis has been placed on the errors arising in activation analysis, it should not be thought that these effects are serious in the majority of analyses. Perhaps the most important general interference is likely to arise from a high neutron absorption cross-section of the sample itself (such conditions in the standard are easily dealt with), but

it is fortunate that many of the common matrix materials, silicon, oxygen, carbon, hydrogen, aluminium and iron, have low total absorption cross-sections for neutrons of thermal and intermediate energies.

Activation analysis has the following advantages:

(1) For a wide variety of elements (some seventy elements have been investigated and a useful bibliography is available[14]) the sensitivity is high and is amenable to simple calculation (a comparison of the sensitivities of other methods of trace analysis with radioactivation has also been made[15]).

(2) The specificity is high, since a chemical process can be devised which is unique for the element in question, and the success of the operation can be checked by measurements of the half-life and β- and γ-ray energies of the radioisotope concerned.

(3) The method is free from reagent blank corrections, as only the constituents of the irradiated sample will be radioactive and only the radioactive content is determined.

(4) There is in general little interference from the matrix with the requirements for special standards.

(5) The chemical procedure need not be quantitative.

(6) The chemical manipulations are carried out with semi-micro amounts of carrier (*e.g.*, 10–50 mg) rather than with micro- and submicrogram amounts.

On the debit side of the ledger we have the following facts:

(1) Few laboratories have suitable irradiation facilities within immediate reach of a reactor, a fact which restricts the use of the method when short-lived isotopes only are formed.

(2) Certain samples cannot be accepted as they might endanger the safety of the reactor, *e.g.*, volatile organic liquids which might decompose under the action of the intense gamma and neutron bombardment, building up dangerous pressures in the sealed sample containers.

(3) Certain matrices become highly radioactive, emitting penetrating radiation, so that the facilities of a laboratory suitable for handling relatively high levels of radioactive materials are required.

It can be seen that the objections to the method are not very restrictive, and although it is unfortunate that several important elements such as oxygen, carbon, nitrogen, and fluorine cannot be analysed adequately, the application to other elements is a powerful addition to the analytical armoury.

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DISCUSSION

J. Hoste (*Belgium*): Have you any experience in the use of γ-spectrometers to suppress or compensate for Compton effects, which obscure results where a mixture of gamma energies is involved?

G. B. Cook (*U.K.*): We have little experience of coincidence arrangements using the two-crystal systems of the Pierson type. I believe they are of little advantage in purely quantitative work. Single-crystal systems have proved adequate for our needs.

D. Gibbons (*U.K.*): We consider that the extra time required to match up the responses of the anthracene and sodium iodide crystals used in the Compton-effect subtraction spectrometer of the Pierson type, and the increased statistical error involved, more than offset the advantages of the system compared with techniques using simple radiochemical separations in combination with single-channel spectrometry. The double-crystal system is excellent for qualitative work where it is necessary to identify, say, five gamma-emitting impurities, but their actual separation and quantitative measurement are best done by chemical processes.

We have also used coincidence spectrometry, not for the purpose of suppressing Compton effects, but for measuring radioisotopes emitting similar gamma energies. Although the technique is very useful for such purposes, its sensitivity is not great because its overall efficiency is the product of the efficiencies of the two detectors.

P. LEVEQUE (*France*): In the quantitative determination of radioisotopes, using either single or multi-channel gamma spectrometers, was the quantity determined on the basis of peak heights or peak areas, and how were the highest-energy Compton effects compensated for?

What experimental set-up was used to avoid the many corrections needed in determining beta activity? In France, a filter-paper method of preparing the specimens and standard samples has overcome many difficulties; the same correction for self-absorption could be applied to both.

It has been found in France that the results over a series of determinations on a given material varied by more than the statistical counting error. I wonder whether, in using very small samples as suggested in the paper, there is not a considerable error, arising from non-homogeneity of the sample, which is superimposed on the statistical counting error, so that the results are less precise than expected.

G. B. COOK (*U.K.*): Determination methods using peak height and peak area have been compared, and the peak-height determination has been found to yield a higher overall variation. The peak-area determination method is therefore better.

The high-energy Compton effect is compensated for by the empirical method of extrapolating from before to after the Compton-effect peak.

The samples are usually mounted by means of a suspension or slurry of the precipitates in a suitable solvent. The suspension is poured onto an aluminium tray and the solvent is evaporated off. For many substances, this method produces a good uniform layer; an important exception is silver chloride. The coagulated precipitate normally used does not meet the needs of the radiochemist, and in connection with fission products analysis a modified technique has been developed to produce finely divided silver chloride which gives the uniform precipitate required for beta-particle analysis.

The filter-paper method has also been used in the United Kingdom and has been found to give a uniform area of precipitate.

I agree that the overall error in the determination of uranium by fission-products analysis is given as 0·5 per cent against an expected statistical error of 0·4 per cent. Clearly there are still a number of uncontrollable factors involved, and the remedy is to exercise careful attention to detail throughout the process. In addition to statistical randomness, it is necessary to take into account randomness on the part of the analyst, perhaps particularly when, as frequently happens, radioactivation analysis is performed by physicists, who are not necessarily fully conversant with the techniques of chemical analysis.

H. SELIGMAN (*I.A.E.A.*): I believe that the errors mentioned in the paper often depend on the availability of fast neutrons, which varies from reactor to reactor and also from place to place within a given reactor.

Has any radioactivation analysis work been done with fast neutrons only, in order to obtain (n,α) and (n,p) reactions, particularly the latter? Very large fluxes would, of course, be needed, but such fluxes should now be available.

G. B. Cook (*U.K.*): In the graphite-moderated reactor, there is a rapid (exponential) fall of the fast/slow neutron ratio in the reflector to the edge of the biological shield. Thus it is possible to find irradiation positions where the fast-neutron flux is very low, but the slow flux is also so low that it is doubtful whether sufficient sensitivity could be secured. In the heavy-water-moderated reactor all irradiation positions are in the reflector. Fluxes of 5×10^{12} neutrons cm^{-2} sec^{-1} to less than 1×10^{12} neutrons cm^{-2} sec^{-1} are obtainable.

I have no special experience with very high fast-neutron fluxes, except with the flux in B.E.P.O., which, in any case, is not particularly high for the ^{32}S (n,p) ^{32}P technique.

A. H. W. Aten (*Netherlands*): The correction for the Compton continuum in gamma spectra is not an important point in radioactivation analysis applications, since the observed spectrum only has to be interpreted as the sum of the essentially known spectra of the various pure components. It is, however, very important in determining the energy and intensity of gamma spectral lines. A satisfactory technique has been developed by overall measurement of a series of long-lived standard nuclides (*e.g.*, ^{203}Hg, ^{137}Cs, ^{54}Mn, ^{65}Zn and ^{22}Na), from which the shape of substantially pure gamma lines may be obtained. Starting with the line of highest energy, each gamma-line is "peeled off" in turn by adjusting the shape of the photo-peak to the observed standard shape and subtracting the Compton contribution. The method permits as many as fifteen gamma lines in a single spectrum to be "peeled off" and is very accurate, provided that great attention is paid to the purity of the calibrated nuclides and also to the stability of the instruments.

Back-scatter peaks due to the different physical forms of specimens are avoided by ensuring that as many aspects as possible of the experimental arrangement are reproducible. The samples should be kept small and in the same position, and it is especially important that the electronic instruments employed should be reliable so that there are no changes of sensitivity during the measurements.

P. Leveque (*France*): In a recent publication of mine on the determination of uranium a correction has been made for the products of fast neutron fission of ^{238}U. Applying this method to the figures given in a United Kingdom paper on uranium determination, I have calculated that the fast-neutron flux in B.E.P.O. is about 12 per cent of the thermal flux.

G. B. Cook (*U.K.*): We have calculated the fast thermal flux ratio by determining the slow neutron flux using the $^{23}Na(n,\gamma)^{24}Na$ reaction and the fast neutron flux using either the $^{32}S(n,p)^{32}P$ or $^{58}Ni(n,p)^{58}Co$ reactions. The fast thermal ratio was 17–20 per cent.

W. W. Meinke (*U.S.A.*): The point raised about the counting error being greater than the statistical error is at least partly explicable in terms of random behaviour of the electronic apparatus. Results begin to exceed the statistical deviation after samples have been irradiated for several hours.

Dr Cook has pointed out that many laboratories do not have ready access to neutron sources, which is an important disadvantage when the radionuclides to be determined have short half-lives. I should like to draw

attention to the fact that certain companies in the United States and the United Kingdom are developing neutron generators based on the reaction of deuterons of relatively low energy on tritium to give essentially mono-energetic neutrons of 14 MeV with a flux after thermalization of about 10^9 neutrons cm^{-2} sec^{-1}, which is sufficient to induce measurable activation of microgramme quantities of such elements as vanadium. The same reaction has been used for some years but on relatively large and costly Van de Graaf machines. New compact neutron generators will shortly be available at a price (about US$20,000) comparable with that of a good mass spectrometer and, of course, much lower than that of reactors. The targets are of tritium adsorbed on zirconium foil and sealed in generator tubes which have a life of several hundreds of hours, sufficing for many kinds of work though not for work involving irradiation for several weeks. A replacement tube will cost about US$500.

With regard to Dr Seligman's request for information about fast neutron activation, a paper by Turner in *Analytical Chemistry* describes the use of 14 MeV neutrons to induce (n,p) reactions in aluminium and silicon. A similar process applied to oxygen in water has also been described by Fall of Harwell.

G. W. Reed (*U.S.A.*): Concerning the question by Dr Seligman on the application of fast neutrons in activation studies I should like to offer the following.

At the Argonne National Laboratory we have facilities in the CP-5 heavy-water reactor which permit

(1) irradiations with almost purely thermal neutrons inside the graphite moderator;
(2) irradiations at higher fluxes and with a high percentage of epi-thermal neutrons in thimbles adjacent to fuel rods; and
(3) irradiations inside a specially constructed fuel element where maximum fission spectrum (unmoderated) neutrons are available.

We have used this last facility to measure the amount of ^{204}Pb in meteorites *via* the reaction

$$^{204}Pb(n,2n)^{203}Pb \xrightarrow{\epsilon,\ e^-,\ \gamma} {}^{203}Tl$$

Since ^{208}Pb gives ^{209}Pb *via* (n,γ) we are thus able to measure the $^{208}Pb/^{204}Pb$ ratio.

The sensitivity is about 10^{-6} g/g. That is, enough activity is produced in 10^{-6} g of lead in this type of irradiation (the thermal flux is about 2×10^{13} neutrons cm^{-2} sec^{-1}) to be determined with a small overall counting error. The radiations are measured both *via* beta and scintillation counting. A monitor is always measured simultaneously so that a quantitative determination is made. The results obtained by both counting techniques agree quite well.

One critical aspect of the lead measurements lies in the timing. Exhaustive chemistry was necessary—and time consuming—since ^{209}Pb ($t_{\frac{1}{2}} = 3{\cdot}3$ h) can only be measured from its beta activity. ^{203}Pb decays by orbital electron capture, and photons, as well as conversion electrons, were measured. Samples counted were always less than 0·8 mg/cm^2 to

avoid the necessity for making self-absorption corrections. Some of the results are compared with mass spectrometrically measured ratios in *Tables 1* and *2*. The errors associated with the ratios are larger than our statistical errors, possibly because of systematic errors, inhomogeneity in samples, *etc.*

Table 1. Lead in sulphide phase of iron meteorites
(Concentrations in g/10^8 g of sample)

Activation analysis	^{204}Pb	^{206}Pb	$^{206}Pb/^{204}Pb$
Canyon Diablo	9·2 ± 0·1	267 ± 2	28·8 ± 1·0
	10·5 ± 0·2	293 ± 3	27·6 ± 1·0
Toluca	10·8 ± 0·2	311 ± 6	28·8 ± 3·1
			28·2 ± 0·7
Mass spectrometry[*]			
Canyon Diablo		1050	29·44
Henbury		292	29·54
			29·49

[*] Claire Patterson, "Age of meteorites and the earth", *Geochim. et Cosmochim. Acta*, **10**, 230 (1956).

Table 2. Isotopic composition of lead in some chondritic meteorites

Meteorite	$^{206}Pb/^{204}Pb$	*Literature*[*]
Nuevo Laredo	59 ± 8	67·97
Indarch	26·8 ± 1·2	
Mighei	31·1 ± 1·2	
Orguiel	30·3 ± 1·2	
Average Troilite	28·2 ± 0·7	29·49

[*] Claire Patterson, "Age of meteorites and the earth", *Geochim. et Cosmochim. Acta*, **10**, 230 (1956).

K. LJUNGGREN (*Sweden*): In addition to the Pierson method of Compton-effect suppression mentioned by Dr Hoste, more sensitive spectrometry may be secured by the use of a fairly fast coincidence circuit with a resolving time of 10^{-8} to 10^{-7} sec for measuring cascaded gamma rays and also for determining positron emitters.

Has Dr Cook any figures on the ultimate accuracy of radioactivation analysis?

G. B. COOK (*U.K.*): An error of ±5 per cent is an accepted accuracy. This figure may be improved upon in very special circumstances, but that is not to be expected from an analysis technique which it is hoped to make into a routine service.

A. H. W. ATEN (*Netherlands*): Reference has been made to the measurement of the fast neutron flux in a reactor by the (n,p) reaction on sulphur ($^{32}S(n,p)^{32}P$). In this connection it may be of some interest to know that the use of the (n,p) reaction on phosphorus-31 gives identical results.

However, the short half-life of ^{31}Si makes this reaction much more sensitive for short irradiations. The ratio of the cross-sections has been checked by irradiating samples of sulphur and phosphorus in different activation positions, and found to be quite constant throughout the reactor. Thus, the P–Si reaction could be substituted for the S–P reaction in all cases, and with advantage where short irradiations are concerned.

G. W. Leddicotte (*U.S.A.*): The facilities available to the analytical chemist at Oak Ridge provide a total flux of the order of 10^{12} neutrons cm^{-2} sec^{-1} in the graphite reactor and 10^{14} to 10^{15} neutrons cm^{-2} sec^{-1} in the O.R. research reactor.

With regard to the fast (epi-cadmium and above) neutron flux, the two reactors provide fluxes of the order of 10^{9} and 10^{12} neutrons cm^{-2} sec^{-1} respectively at an energy of 2·3 MeV, 5×10^{8} and 1×10^{11} neutrons cm^{-2} sec^{-1} respectively at 6·8 MeV, and 10^{8} and 10^{10} neutrons cm^{-2} sec^{-1} respectively at 8·3 MeV and above. These fluxes are used for the determination of nickel and titanium.

With regard to γ-spectrometry, Oak Ridge is using a crystal gamma discriminatory system with two crystals, not of different substances but both of sodium iodide of differing thickness. By permitting loss of high energies, the wafer crystal emphasizes the low energies. Used with multichannel analysers, the system can be employed for the semi-quantitative analysis of various constructional materials and seems to be quite a promising technique.

I agree with Dr Cook that ± 5 per cent is generally acceptable as an indication of the accuracy of the method, but in many cases a larger error must be accepted.

Ph. Albert (*France*): I wonder if there is an irradiation position in a reactor where the (n,α) reaction for the determination of sodium in aluminium does not occur. Using extremely pure "zone-melted" aluminium, we have observed in the El.2 reactor at Saclay that an apparent sodium content of 0·2 parts/million could be measured, and we wonder whether this value represented the extent of occurence of the (n,α) reaction, or the minimum concentration of sodium in "zone-melted" aluminium.

With regard to the determination of sulphur by the $^{32}S(n,p)^{32}P$ reaction, it has been stated that not only phosphorus but also chlorine could be a substantial source of error, as it, too, yielded phosphorus-32 ($^{35}Cl(n,\alpha)^{32}P$).

In connection with the determination of elements with low effective cross-sections for neutrons, or excessively short half-lives, Gill at Harwell has determined boron in silicon by protons and Albert and Sue have determined carbon in iron and aluminium by deuterons. This indicates, I think, that the use of accelerators—not necessarily very powerful ones—by chemists is a promising line of work. It seems that oxygen, carbon and nitrogen might be determined with great sensitivity in this way.

The possible errors, referred to by Dr Leveque, due to heterogeneity of the samples may be avoided by using fairly large samples (about 1 g) and subsequently performing the analysis on aliquot parts.

F. Girardi (*Italy*): The use of plastics such as nylon and polythene for the capsules containing the samples has given rise to much difficulty at

Chalk River, especially with sulphur and phosphorus determinations, because they strongly adsorb active material from the target. Nylon capsules have in some cases acquired an activity of more than 10,000 counts/min.

I agree with the statement that the presence of chlorine might interfere with sulphur determination using the $^{32}S(n,p)^{32}P$ reaction. The effective cross-section for the latter has been measured at Chalk River as 2·0 mb; thus the effective cross-section for the $^{35}Cl(n,\alpha)^{32}P$ reaction of 0·79–0·8 mb is relatively large.

G. B. Cook (*U.K.*): I have used polythene capsules for short irradiations in a reactor without particular difficulty, though I agree that their use is restricted. Quartz capsules are used for longer exposures.

I agree about the interference of chlorine with sulphur determinations which represents a further disadvantage of the $^{32}S(n,p)^{32}P$ reaction in addition to the ^{31}P interference mentioned in my paper.

D. Mapper (*U.K.*): May I refer Dr Albert to the paper by L. Salmon* entitled: " The extent of the fast neutron effect on the determination of sodium in aluminium by activation in the Harwell pile "?

Reverting to the merits of gamma-spectrometry, it is clear that during this conference the relative advantages of gamma-spectrometry, with and without radiochemical separation will be discussed extensively. We are particularly concerned with the determination of traces of many elements, whose gamma-emitting intensities are minute compared with the gross gamma-activity in the bulk of the sample. In such cases radiochemical separations *must* be performed. Even in the case of a simple determination like that of arsenic in very pure silicon, it has been shown† that the contributions to the measured ^{76}As photo-peak from ^{122}Sb and ^{64}Cu, due to the presence of antimony and copper, could introduce serious errors, even though the decay of the photo-peak is followed for some time, if the determination is made entirely without previous radiochemical separations.

In order to eliminate the Compton continuum, the Harwell group uses large crystals, which minimize the Compton effect and increase the photo-peak.

C. Garavelli (*Italy*): I have found that the error in peak-height determination is about 15 per cent, whereas in the case of peak-area determination it is 6–8 per cent. If the curve is obtained without a rate-meter by interpolation between the plots representing the number of counts detected on each channel, about half the overall variation is due to the uncertainty of interpolation.

D. Gibbons (*U.K.*): We have also found that simple peak-height measurements give an error of 10–15 per cent, scaler measurements give 7–10 per cent and peak-area measurements 5 per cent or even better, depending on the stability of the equipment used.

* *A.E.R.E. C/R*.1324 (1954).

† A. D. Smales, D. Mapper, A. J. Wood and L. Salmon. " The determination by radioactivation of trace quantities of arsenic, antimony and copper in pure silicon ", *A.E.R.E. C/R* 2254, (1957).

J. COLARD (*Belgium*): We have used activation analysis and gamma spectrometry for the measurement of small quantities of impurities of the order of parts per million, in liquids. Traces of vanadium and sodium in mineral oils in various stages of purification have been measured. Chemical manipulations on the samples were avoided, both before irradiation, so as not to introduce further impurities, and after irradiation in view of the short half-life of vanadium-52 (3·76 min). Gamma spectrometry has been used in order to avoid interference from other impurities.

We have found the limit of detection for vanadium to be 0·005 parts/million using a sample of 10 cm^3 which has been irradiated for 5 min at a flux of 2×10^{12} neutrons cm^{-2} sec^{-1}. The limits for sodium and manganese were found to be 0·05 parts/million and 0·007 parts/million respectively. The reproducibility at these limits is about 25 per cent and 5–10 per cent for higher concentrations.

SPECTROMETER FOR THE DETERMINATION OF POSITRON AND GAMMA-RAY CASCADE-EMITTING NUCLIDES

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Un spectrometre de coincidence à trois-voies pour la détermination des nuclides qui emettent des positrons ou des cascades de rayons-gamma est décrit. Quelques examples de son utilisation dans les analyses de radioactivation sont donnés.

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The general procedure in activation analysis work is to separate chemically the elements to be determined. In many cases, however, the results can be obtained more quickly by using the spectral distribution of the radiations emitted. This can be done by spectrometry, either on the irradiated sample itself, in favourable cases, or after a simple chemical separation into groups of elements. The spectrometric or non-destructive activation analysis technique has reached a state of high development with the introduction of multi-channel analysers. It is now possible to make measurements on individual gamma components down to 10^{-11} curies, and also on rapidly-decaying nuclides. The interpretation of composite gamma spectra has also been made much easier by various subtraction methods which suppress the Compton distribution or facilitate the consecutive analysis, nuclide for nuclide, of the registered spectra.

Another property of emitted radiations which has not been fully exploited for activation analysis measurements is the time relation between successive quanta or particles emitted by one and the same nucleus. In the great majority of cases the decay of a nucleus involves the emission of more than one particle or photon. The study of these decay properties has led nuclear physicists to the development of an extremely refined measurement technique, based upon the coincidence principle. The principles of coincidence theory and practice are well known, and the different circuits and their data have been dealt with extensively in the literature. Here we need only stress the importance of the scintillation detector in this connection and in nuclear spectrometry. This detector permits milli-microsecond resolving times in the coincidence circuits and has made studies of life-times down to 10^{-11} sec possible. The theory and techniques of the fast coincidence circuits have been excellently reviewed by Bay[1].

The importance of fast or medium-speed coincidence circuits for the measurements encountered in spectrometric activation analysis work, *i.e.*, selective measurement of one nuclide in a mixture of nuclides, lies in the increased selectivity which can be achieved if the measurement equipment not only selects the required radiation with respect to energy, but also accepts only such signals as are related in a certain way in time. The latter usually means that the signals from two detectors viewing the active source should be simultaneous within a short time interval—the resolution-time

constant. As the ratio of genuine coincidences to randomly occurring, unwanted coincidence events is improved with a decreasing time constant, the circuits used should be as fast as possible.

Coincidence techniques can be applied to beta–gamma decay, gamma–gamma cascades, and positron annihilation. The present report deals with some preliminary results obtained in measurements on ^{60}Co, which is characterized by a gamma-ray cascade with energies of 1·17 MeV and 1·33 MeV respectively, and ^{64}Cu, which is a positron emitter. For the measurements a coincidence spectrometer, based on the post-coincidence energy selection principle originated by Bell and Petch[2] was used. The principle of the circuit is shown in *Figure 1*.

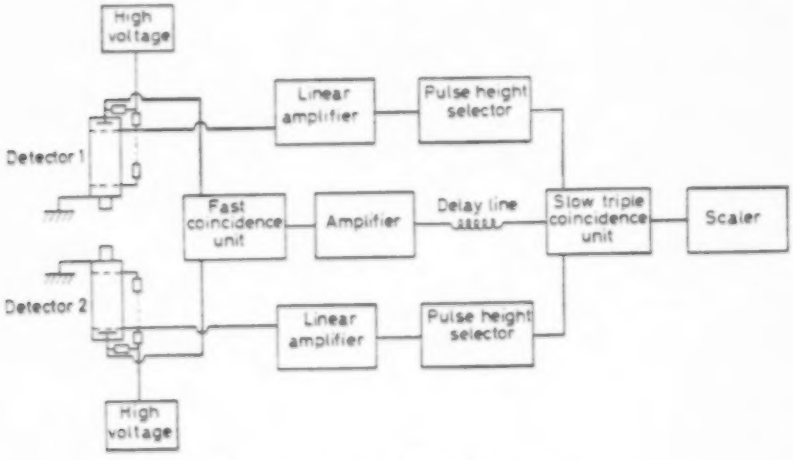

Figure 1. Fast-coincidence spectrometer

The pulses from the two detectors are fed directly to a fast-coincidence stage. After a certain delay, the coincident output pulses are fed to a slower triple-coincidence unit, where they meet pulses which have been analysed in energy in the ordinary way in a differential discriminator after the necessary amplification in a linear amplifier. If the time delay in the fast channel is properly adjusted, coincidences between all three channels will be recorded when the absorbed photons in the two crystals: (1) have the pre-selected energies set in the single-channel analysers, and (2) are simultaneous within the time-interval set in the fast-coincidence unit. Since resolution is independent of what happens in the side channel, the time necessary for pulse-height analysis will not limit the speed of the circuit. If sodium iodide is used as scintillator (it is suitable—as usual—because of its high gamma-absorption efficiency), the resolving time of this type of circuit may still be as short as 10^{-8} sec. Many different circuits can be used in the fast-coincidence stage. The present circuit is based on designs given by Azuma and Lewis[3] and Macq and Vervier[4]. The collector signal from the photomultiplier cuts off a heavily-conducting high-transconductance tube (actually two E180F's in parallel are used to increase the current).

The anode current is diverted into the coaxial cable (HH 1500) which is connected as anode load. The resulting positive voltage pulse is clipped by a short-circuited cable of suitable length and then applied to one of the control grids of a 6BN6 gated-beam tube, while the other control grid receives pulses from the other photomultiplier through an identical circuit. The 6BN6 tube gives no anode output unless both control grids are operated simultaneously by positive-going pulses. The 6BN6 tube coincidence circuit, introduced by Fischer and Marshall[5], is capable of very short resolving times.

The present investigation has been carried out as a comparison between a medium-speed energy selective two-channel system with a resolving time $t = 100$ mμsec and a high-speed three-channel system with $t = 28$ mμsec. The nuclides ^{64}Cu and ^{60}Co have been chosen as examples of positron and gamma cascade emitters because their determination is often of interest in biological and technical problems. They are frequently accompanied by a heavy background of other radiation in irradiated samples. As typical examples, a disturbing activity of ^{24}Na is assumed to accompany the copper activity to provide an illustration of conditions occurring in biological samples, and a disturbing activity of ^{59}Fe (which has metallurgical significance) is assumed to be present together with the cobalt activity. The circuit was therefore set to accept the ^{64}Cu and ^{60}Co radiations under optimal conditions in two different runs. With the settings for the copper annihilation radiation, measurements were also made on ^{24}Na and ^{137}Cs. In the same way, a ^{59}Fe source was measured with the circuit set to accept the two photo-peaks at 1·17 and 1·33 MeV in the side channels. The results have been collected in *Table 1*.

Table 1

(Source: crystal spacing = 1·6 cm)

	Sensitivity (counts min^{-1} μc^{-1})*					*Selectivity ratios*		
	^{64}Cu	^{24}Na	^{137}Cs	^{60}Co	^{59}Fe	^{64}Cu/^{24}Na	^{64}Cu/^{137}Cs	^{60}Co/^{59}Fe
Two channels $t = 100$ mμsec	4500	28	0·13	52	4·8	160	35,000	11
Three channels $t = 28$ mμsec	4000	22	0·034	49	0·93	180	120,000	52

*The sensitivities given for ^{59}Fe and ^{137}Cs refer to source strengths of approximately 10 μc.

Some interesting observations can be made from the data in *Table 1*. As is to be expected, the sensitivity for copper is considerably higher than for sodium. However, it can be seen that the sensitivity ratio is very little affected when the resolving time is reduced by switching in the fast channel. The selectivity for copper is mainly accounted for by the energy selection in the side channels. The reason why the number of coincidences does not decrease with the resolving time must be that genuine coincidences appear in the decay of ^{24}Na. This we know to be the case, since ^{24}Na has two cascaded gammas, of energy 2·76 MeV and 1·38 MeV. The part of the Compton distributions that falls in the selected energy channels contains such coincident events.

On the other hand, ^{137}Cs does not have any coincidences of this type. The sensitivity, already low at the long resolving time, decreases further following the reduction in resolving time.

The absolute efficiency for ^{60}Co is considerably lower than for ^{64}Cu. A much lower percentage of the total disintegrations passes by the side channels. The radiation from ^{59}Fe which contains two photo-peaks of nearly the same energy as ^{60}Co, but emitted as alternatives and not in cascade, gives a much lower counting rate. This is further reduced with the resolving time.

We may conclude that the short resolving time has a great bearing on the selectivity of the circuit if the measured source does not contain any coincident radiation of an energy higher than the one selected for the measurement of a given nuclide. If the dominating background is a highly energetic gamma cascade, no improvement will be obtained at lower resolving times.

The sensitivity figure for copper-64 which is given in *Table* 1 corresponds to an overall efficiency of 2×10^{-3}). The copper efficiency can be increased by using a smaller distance and broader channels, and the resolving time can presumably be reduced to near 10 mμsec without undue loss of overall sensitivity. Further studies will be made of the optimal circuit parameters in different measuring problems, and of modifications required in the circuit itself to improve its characteristics. One difficulty is already apparent: the photomultiplier gain will vary with the source strength presented to the detectors. This will change the settings of the single-channel pulse-height selectors with the background accompanying the nuclide measured. A different photomultiplier might have to be used, or else a diode-type fast-coincidence circuit might be used instead of the existing one, since the diode-type circuit operates at a lower voltage level. The photomultiplier could thus be run at a lower voltage, where stability problems are less serious. Furthermore, the total activity that can be presented to the counters is limited to around 10 μc with the efficiencies specified here.

Addendum

Recently, a very interesting development in the field of coincidence spectrometers has been published by Hoogenboom[6]. This instrument should be very useful for the measurement of irradiated activation analysis samples.

The iron standard by means of which the sensitivity and selectivity data given above were obtained contains a certain amount of cobalt, as established in later measurements. The cobalt content is about 10 parts/million. With a new ^{59}Fe standard practically free from cobalt new values for the selectivity of the circuit for ^{60}Co relative to ^{59}Fe were obtained: 16 and 140 at resolving times of 100 mμsec and 28 mμsec respectively.

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NEUTRON ACTIVATION APPLIED TO GEOCHEMISTRY

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Au cours des dernières années, on a constaté que l'analyse par radioactivation est un moyen très efficace d'étudier les problèmes fondamentaux qui se posent en géochimie et en cosmochimie. L'auteur décrit les travaux récents accomplis dans ce domaine, et les remarquables possibilités qu'offre cette méthode. L'un des grands avantages de l'analyse par radioactivation est qu'elle permet souvent d'obtenir simultanément des renseignements sur la quantité des éléments présents à l'état de traces et sur leur composition isotopique. Une attention particulière sera accordée aux techniques nouvelles de traitement des gaz et des substances volatiles. Les recherches sur la répartition et l'abondance des éléments à l'état de traces, notamment les problèmes concernant la détermination de l'âge géologique des minéraux et des météorites présentent un intérêt croissant. La mesure du rapport K/Ar donne des résultats excellents lorsqu'elle est fondée sur la radioactivité induite de ^{41}Ar et de ^{37}Ar. On peut également appliquer l'activation neutronique aux méthodes classiques de détermination du rapport Rb/Sr et du rapport U/Pb. On peut recueillir des données utiles sur les radioactivités naturelles d'éléments tels que le ^{176}Lu et le ^{187}Re et sur leurs possibilités d'application aux problèmes géologiques. Dans les recherches sur les météorites, " l'activation neutronique " sert surtout de moyen d'analyse. Dans ce cas, des éléments à l'état de traces qui présentent un intérêt ont une concentration comprise entre 10^{-7} et 10^{-10} g/g; on peut aussi déceler les produits stables de spallation tels que ^{3}He, ^{6}Li, K, ^{45}Sc, *etc.* formés par l'action des rayons cosmiques. Ces données analytiques permettent de mieux connaître le spectre énergétique et la constance du rayonnement cosmique dans le temps. On peut en déduire l'âge " radiologique " et l'âge-matière des météorites.

The discovery of radioactivity has stimulated research in the natural sciences and especially in geology. Radioactive atoms have helped to solve two independent but related problems, the establishment of the geological time scale and the determination of the heat balance and geological and cosmological abundance of elements.

Only sixty years ago an English geologist, W. J. Sollas, remarked in his book entitled *The Age of the Earth*: " How enormous would be the progress in our science if it were possible to relate the important events of our earth-history to a time-scale " . . . and he continues: " Until now, this has often been tried but in every case the hope sublimed away. Nevertheless I do trust that one day a talisman will be found to enable geological dating."

By this time the still " unknown " talisman had already been discovered in the existence of the radioactive elements. Nature had built her own clock.

Here it may be of interest to remember that William Thomson, later Lord Kelvin, was the first to make an attempt to help the geologists with physical methods. Kelvin was convinced that the sun and also the earth were subject to the same physical laws of cooling. He calculated that at one time the earth had cooled according to these laws and that life could

exist no earlier than some 20 million years ago. Concerning the future he pointed out that the cooling of our earth is continuing, and therefore life is limited in time, and very cautiously he added: " in case there is not a new source of energy in nature still unknown to us." It is surprising that this argument was never seriously considered and the controversy about the possible age of the earth continued for many years.

It was in 1903 that Pierre Curie and Laborde made their famous experiment measuring the heat developed directly by radium. Shortly after this Strutt showed that radium is distributed in all minerals of the earth's crust, the amounts being large enough to balance the cooling.

Consequently all earlier calculations about the cooling time of the earth were incorrect.

Table 1. Primary natural radionuclides

Nuclide	*Isotope abundance* (%)	*Type of disintegration*	*Half-life* (years)	*Stable end-products*
^{235}U	0·715	α	$7{\cdot}1 \times 10^{8}$	^{207}Pb, ^{4}He
^{40}K	0·012	β (88%), ϵ (11%)	$1{\cdot}3 \times 10^{9}$	^{40}Ca, ^{40}Ar
^{238}U	99·28	α	$4{\cdot}5 \times 10^{9}$	^{206}Pb, ^{4}He
^{232}Th	100	α	$1{\cdot}4 \times 10^{10}$	^{208}Pb, ^{4}He
^{176}Lu	2·60	β	$2{\cdot}2 \times 10^{10}$	^{176}Hf
^{87}Rb	27·8	β	$5{\cdot}0 \times 10^{10}$	^{87}Sr
^{187}Re	62·9	β	$6{\cdot}3 \times 10^{10}$	^{187}Os
^{147}Sm	15·1	α	$1{\cdot}3 \times 10^{11}$	^{143}Nd, ^{4}He
^{138}La	0·089	ϵ (90%), β (10%)	2×10^{11}	^{138}Ba, ^{138}Ce
^{190}Pt	0·012	α	5×10^{11}	^{186}Os, ^{4}He
^{115}In	95·8	β	6×10^{14}	^{115}Sn
^{144}Nd	23·9	α	3×10^{15}	^{140}Ce, ^{4}He

I mention these historical events to underline the importance of an exact analysis of the natural radioelements and to show that the problem is still of current interest. For this subtle analytical work new sensitive methods had to be developed. The recent enormous progress in this field is directly related to the progress in nuclear energy. In particular neutron activation techniques have found wide use in geochemistry.

The principle of a radioactive age determination is well known. Using the decay law in the form $N_d = N_m (e^{\lambda t} - 1)$ we have to determine in the same mineral sample the amount of the mother element N_m and the amount of its stable daughter product N_d. From the rate of decay we know the amount of the decay product which is produced in one year. It should then be easy to calculate how many years have passed since the mineral was formed.

Although the principle of the method seems to be quite simple, in practice many difficulties are encountered so that there are only a limited number of age determinations which are absolutely reliable. To explain this we should have a look at *Table 1* where twelve primary natural radionuclides of major interest are given in order of increasing half-lives. These nuclides are not all suitable for age determination. If the half-life is very large, the amount of decay product is too small and the analytical difficulties increase considerably. Also if a gas is produced in the radioactive series,

or is the end product, serious diffusion losses can occur. The rarer elements are applicable only in special cases to dating work. By far the most widely applicable method for a geologist is the potassium–argon dating method. Potassium minerals are most common, and their application is of growing importance in geochemistry. Therefore the work on this nuclide should be mentioned first in demonstrating the usefulness of the neutron activation technique.

The isotope ^{40}K decays in two ways, partly into ^{40}Ar, but mainly (88%) into ^{40}Ca. In potassium minerals practically pure ^{40}Ar occurs. As the neutron capture cross-section for the production of ^{41}Ar ($t_{\frac{1}{2}} = 1{\cdot}8$ h) is relatively high, the limit of detection will be in the range of 10^{-10} g of ^{40}Ar. The competing reaction $^{41}K(n,p)^{41}Ar$ has a comparatively low cross-section

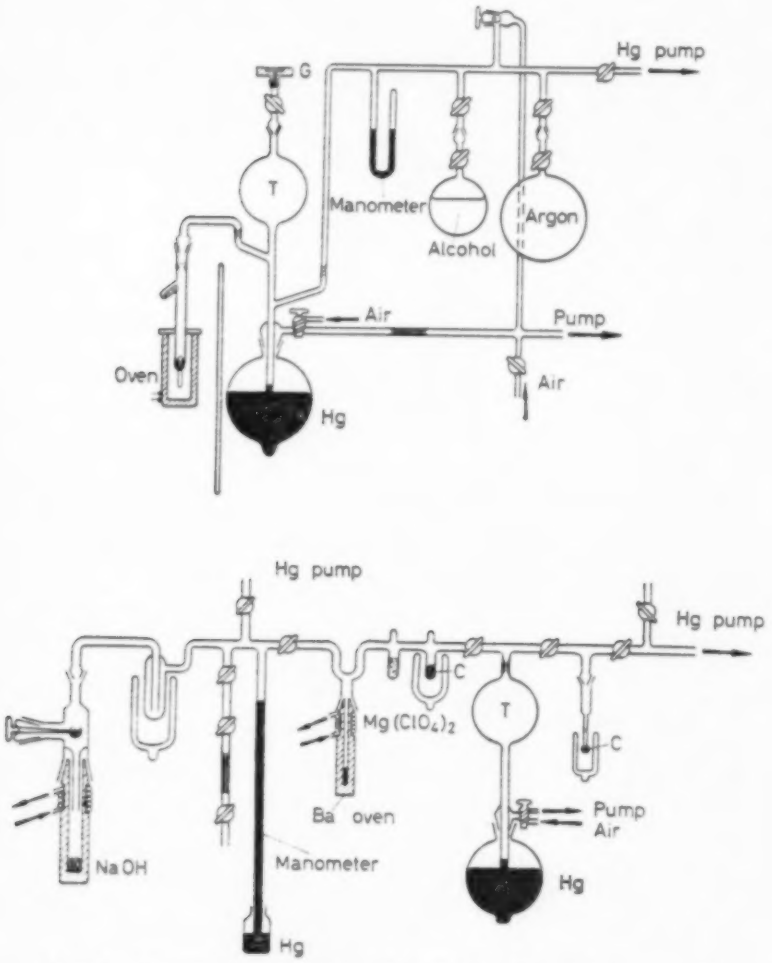

Figure 1. Apparatus for extraction and purification of argon from minerals

and depends largely on the presence of energetic neutrons. Therefore it might be preferable first to isolate quantitatively the argon from the mineral, so making the activation independent of the mineral composition. This would also make possible the investigation of minerals which contain boron, lithium, rare earth elements or other neutron poisons.

The separation of argon from a mineral sample is relatively easy and the procedure is well known. Using neutron activation we have the choice either of isolating the ^{40}Ar quantitatively or of using one of the principles of this technique to measure the yield of recovery after mixing with a known amount of carrier argon gas.

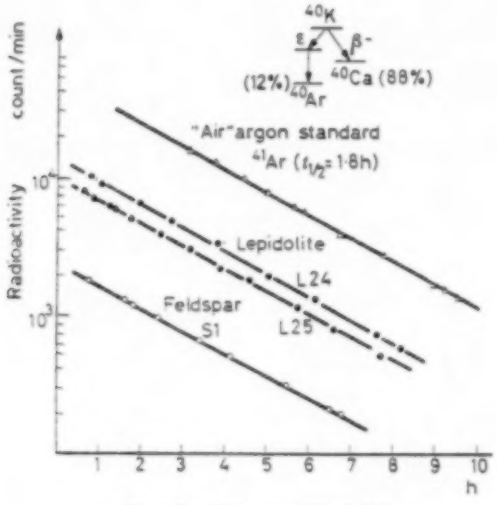

Figure 2. Decay curves of ^{41}Ar

As far as we know the first publication on this subject was by Moljk and co-workers[1] several years ago. We too in Mainz studied the applicability of the activation method to our geochemical work. In *Figure 1* our apparatus for the extraction and measurement of small amounts of argon is shown.

The finely ground mineral (*ca* 2 g) is opened up in a melt of sodium hydroxide, the evolved gas is purified by traps and a barium oven, *etc.*, and finally the gas is condensed onto charcoal (C) in a little quartz ampoule only a few millimetres in diameter and 4 cm in length. Here the extraction must be quantitative. We checked the experimental conditions with a carrier-free tracer, ^{37}Ar (a K-emitter), which can be measured only in a gas counter, whereas ^{41}Ar and also ^{39}Ar (in long irradiations) are energetic β-emitters and do not require internal gas counting. In the upper part of the apparatus the irradiated argon ampoule is broken and the argon brought by means of a Toepler pump (T) to a little counting chamber (G), a metal dish only *ca* 15 mm in diameter, which is closed by a thin foil. The dish with the enclosed gas is brought beneath an ordinary end-window counter and its β-activity is measured, *Figure 2.*

The decay curve of the $^{41}Ar(t_{\frac{1}{2}} = 1{\cdot}8$ h) has practically no tail. As a standard or reference source we use a certain quantity of " air " argon which is treated in the same way. Often in minerals and in the glass apparatus a small amount of " air " argon is absorbed which may affect the results, but this is not serious. " Air " argon contains a small percentage of stable ^{36}Ar so ^{37}Ar ($t_{\frac{1}{2}} = 35$ d) is produced by the reaction $^{36}Ar(n,\gamma)^{37}Ar$. As the ^{37}Ar K-radiation cannot be observed under the window counter, the gas is transferred to an internal gas counter and the result used as a correction for the amount of the " air " argon impurity present. (The correction is mostly small, ~1–3 per cent.) ^{37}Ar is also produced by the $^{40}Ca(n,\alpha)^{37}Ar$ reaction. We used the same apparatus for the determination of small amounts of calcium in minerals. This method of calcium determination is more sensitive and rapid than that using the $^{44}Ca(n,\gamma)^{45}Ca(t_{\frac{1}{2}} = 225$ d) reaction.

The possibility of loss of the argon in minerals by diffusion during the ages is an important question. This calls for a more detailed study of the diffusion process. As neutron activation is not limited to analytical problems I should like to mention briefly this application. Little is known about the ^{37}Ar diffusion constants in specific minerals such as feldspars, lepidolites and stone meteorites, but the results will probably contribute to an understanding of the observed variations due to diffusion losses in estimates of age.

Table 2. Potassium–argon ages by neutron activation (from A. Rassoul[2])

Mineral	*Weight* (g)	^{40}Ar (μg/g)	K (%)	$^{40}Ar/^{40}K$	$10^{-9} \times$ *Mineral age* (years)
Lepidolite L24					
S. Rhodesia	2·4185	2·931		0·373	2·51 ± 0·24
Nolan mine	2·4600	2·921	6·6	0·372	
Alkyat, Bikita	2·4000	2·856		0·364	
Lepidolite L25					
S. Rhodesia					
Bikita mine,	2·4236	2·511	6·4	0·329	
E. Victoria F.	2·4152	2·523		0·331	2·42 ± 0·20
Feldspar 1					
Swaziland, Mba-	2·4205	1·232	5·53	0·187	
bane, S. Africa	2·3960	1·219		0·185	1·86 ± 0·16
Red granite H3	2·4316	0·384	6·64	0·048	
Torset, N. Norway	2·4238	0·385		0·049	0·64 ± 0·05

Table 3. Comparison of rubidium–strontium and potassium–argon ages (from A. Rassoul[2])

Mineral	*Locality*	^{87}Rb (%)	^{87}Sr (%)	($t_{\frac{1}{2}} = 4{\cdot}8 \times 10^{9}$y) $10^{-9} \times$ Rb/Sr *age* (years)	($t_{\frac{1}{2}} = 1{\cdot}30 \times 10^{9}$y) $10^{-9} \times$ K/Ar *age* (years)
Lepidolite 24	S. Rhodesia, Nolan mine, Alkyat, Bikita	0·574	0·0235 0·0232	2·62 ± 0·19	2·51 ± 0·24
Lepidolite 25	S. Rhodesia, Bikita mine, E. Victoria F.	0·436	0·0170 0·0168	2·51 ± 0·17	2·42 ± 0·20

Some of our results[2] in potassium–argon age determinations are shown in *Tables 2* and *3*. These include data for lepidolites and feldspars from South Africa and Norway. The age is found to be in the range of 0·5–2·6 $\times 10^9$ years. The neutron activations were all made in the B.E.P.O. reactor at Harwell and the samples were sent by air to Mainz. The earliest ^{41}Ar measurements could only be done about 10 hours after dispatch from Harwell. The potassium–argon ages and the rubidium–strontium ages are slightly different in the same mineral. These differences might be due to diffusion losses. However, there is also a small uncertainty in the branching ratio and in the decay constants. Further investigation will serve to fix the values of the constants. (The long controversy on the " true " half-life of ^{87}Rb will be recalled.)

The lepidolites attract our attention as they are relatively high in rubidium content and it was possible to compare the rubidium–strontium age with the measured potassium–argon age. Rubidium is easily detected by its 18-day activity. As lepidolites should not be irradiated directly in a pile (there might be shielding effects due to their high lithium content) the potassium together with rubidium and caesium were separated and bombarded with neutrons.

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Table 4. Potassium–argon ages of stone meteorites (from H. Wänke and H. König[3])

Meteorite	$10^6 \times$ Ar *content* (cm^3/g)	$10^3 \times$ K *content* (g/g)	$10^{-9} \times$ K/Ar *age* (years)
Chondrite			
Akaba	45·0 ± 2·7	1·00 ± 0·04	$3{\cdot}58 \pm {}^{0{\cdot}10}_{0{\cdot}12}$
Beddgelert	20·2 ± 5·7	0·77 ± 0·04	$2{\cdot}77 \pm {}^{0{\cdot}37}_{0{\cdot}45}$
Breitscheid	33·1 ± 2·2	0·82 ± 0·03	$3{\cdot}39 \pm {}^{0{\cdot}12}_{0{\cdot}12}$
,,	32·0 ± 3·0	0·82 ± 0·03	$3{\cdot}34 \pm {}^{0{\cdot}20}_{0{\cdot}21}$
Modoc	52·8 ± 2·9	0·83 ± 0·05	$4{\cdot}12 \pm {}^{0{\cdot}13}_{0{\cdot}14}$
,,	57·3 ± 6·3	0·83 ± 0·02	$4{\cdot}25 \pm {}^{0{\cdot}19}_{0{\cdot}21}$
Pultusk	38·2 ± 7·6	0·79 ± 0·05	$3{\cdot}68 \pm {}^{0{\cdot}30}_{0{\cdot}36}$
,,	41·0 ± 7·6	0·75 ± 0·03	$3{\cdot}87 \pm {}^{0{\cdot}28}_{0{\cdot}33}$
Achondrite			
Pasamonte	23·6 ± 4·7	0·34 ± 0·05	$4{\cdot}27 \pm {}^{0{\cdot}37}_{0{\cdot}47}$
Johnstown	0·4	0·01	

It is well known that radiogenic ^{87}Sr is often nearly 100 per cent pure in these minerals. We isolated some milligrams of strontium element by processes which involved ion-exchange techniques and the removal of calcium and barium (using ^{45}Ca and carrier-free ^{89}Sr as a tracer). The isotopic composition of this strontium was determined by induced activities of ^{89}Sr ($t_{\frac{1}{2}} = 30$ d) and ^{87m}Sr ($t_{\frac{1}{2}} = 2{\cdot}8$ h) which were compared with that of " normal " strontium samples. These activities served as indicators for

the presence of " normal " strontium element in the radiogenic product. A high state of chemical purity is necessary.

As we are working in Mainz in two groups on similar problems it is of interest to mention that Dr Wänke[3] recently developed a potassium–argon method for stone meteorites. These meteorites are fairly old and their potassium content is about 0·1 per cent. Therefore the amount of radiogenic ^{40}Ar is relatively high and is scarcely affected by cosmic ray production of argon.

The ^{41}Ar activity can easily be measured after a short (slow) neutron activation of the stone meteorite itself. There will not be severe interference by competing (n,p) nuclear reactions. Now Wänke observed a relatively strong ^{39}Ar activity ($t_{\frac{1}{2}} = 260$ y) resulting from the $^{39}K(n,p)^{39}Ar$ reaction when irradiating the same stone meteorite for a longer time (2 weeks).

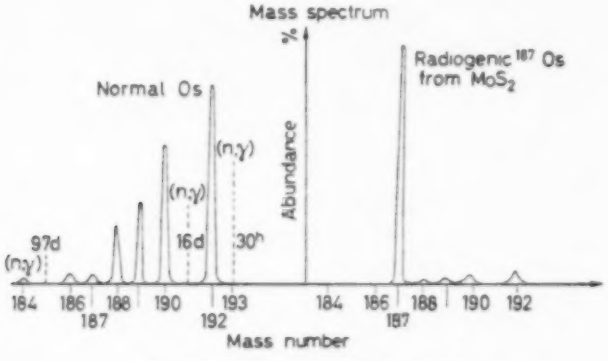

Figure 3. Mass spectrum of osmium

This activity is unaffected by other nuclear reactions and will give directly the amount of potassium present in the sample. Consequently the $^{39}Ar/^{41}Ar$ ratio of activities corresponds to the age of the meteorite. The results are summarized in *Table 4*. They are in good agreement with other facts. Most probably the differences in the age result from diffusion losses in the individual meteorites. The age of the meteorites is found to be in the range of $2{\cdot}8–4{\cdot}25 \times 10^9$ years.

It is worth mentioning that this simple method is similar to the Nier method where lead ages are estimated from the ratio $^{207}Pb/^{206}Pb$, without the necessity of knowing the true lead and uranium contents of the sample. In old minerals this method is by far the most reliable.

Several years ago we started a search[4, 5] for decay products of ^{187}Re the natural β-radioactivity of which was discovered by Libby and Naldrett[6]. In geologically old rhenium-containing molybdenites we found osmium, which from a geochemical point of view should not be in this type of mineral. The results of the mass spectrometric investigation of the isotope abundance of this osmium are shown in *Figure 3*. It clearly shows that one isotope, namely the rare isotope ^{187}Os is the only one present. From this result it seemed clear that the half-life of ^{187}Re had to be corrected considerably.

We tried to evaluate the ^{187}Re half-life by analytical methods[7, 8] in order to determine the traces of rhenium and ^{187}Os and to evaluate the age of the minerals by conventional means. Considerable difficulties were encountered because the molybdenites concerned were not found together with other natural radioelements. We had to establish a " relative " age scale, and tried to relate this to the known geological facts in the history of the deposits.

The trace elements rhenium and osmium were always present in concentrations of 10^{-4} to 10^{-7} g/g of mineral. In the case of rhenium this was determined by neutron activation, but for the radiogenic osmium we had to combine the conventional chemical analysis with neutron activation

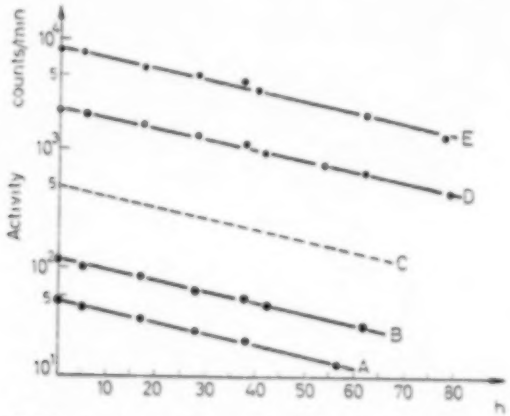

Figure 4. Rate of disintegration of different osmium samples after neutron activation: A, 1·08 μg of Os from Stavanger MoS_2, containing 0·0150 μg (= 1·4%) of normal Os; B, 1·12 μg of Os from " Lofoten " MoS_2, containing 0·034 μg (= 3·0%) of normal Os; C, theoretical 1·33-day disintegration of ^{193}Os; D, 0·8 μg of " normal " Os; E, 4·13 μg of Os containing 2·8 μg (= 68%) of " normal " Os

techniques. The reason was that the isotope ^{187}Os after neutron capture produces ^{188}Os which is stable. However, there was a way to determine the ^{187}Os concentration indirectly. The chemical amount of osmium element present in the sample having been established, the ^{187}Os abundance was deduced from the reduction in the specific radioactivity of the induced radioisotopes ^{191}Os, ^{193}Os and ^{185}Os. The activation method has the advantage that the amounts of osmium required are very small, only in the order of micrograms. (For the first mass spectrometric investigation some hundreds of micrograms were needed.)

Figure 4 shows the results obtained from the activation analysis for radiogenic ^{187}Os in osmium. The limit of detection of normal osmium is of the order of 10^{-3} μg, therefore in highly enriched ^{187}Os an impurity of " normal " osmium is easily detected.

Recently we continued this study in meteorites and it seems to be of interest. Previous attempts to determine the geological age of iron meteorites, for instance by Paneth and co-workers using the helium method, failed, because more recent investigations have shown that an appreciable

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amount of helium consists of helium-3 (~25 per cent) which is due to cosmic ray effects. Moreover, the uranium content of the iron meteorites was shown to be less than 10^{-10} g/g. This latter information is due largely to Reed and Turkevich[9]. In consequence, it is now clear that an age determination based on the decay of uranium and thorium is not feasible. Another attempt made recently by Stoenner and Zähringer[10] with the potassium–argon method using the neutron activation technique gives results which are difficult to understand. The rhenium and osmium contents in some iron meteorites found by neutron activation are given in *Table 5*.

Table 5. Osmium and rhenium contents in iron meteorites (from W. Herr, W. Hoffmeister and L. Langhoff[21])

Iron meteorite	$10^6 \times$ Os *content* (g/g)	$10^6 \times$ Re *content* (g/g)	$10^6 \times$ Re *content** (g/g)	$^{187}Os/^{186}Os$ *ratio*†
Tocopilla	1·29	0·25		1·410 ± 0·012
Henbury	2·25	0·21	1·4	
Canon Diablo	2·07	0·25	0·28	1·127 ± 0·015
Odessa (Fe)	2·61	0·25		
Sichote Alin	<0·02	≪0·01		
Xiquipilco	2·54	0·22	0·25	1·064 ± 0·016
Terrestr. Os–Ir (Ural)	—	—	—	1·025 ± 0·009

* Comparable results from E. D. Goldberg and H. Brown[20].
† Results from J. Geiss, B. Hirt, W. Herr, E. Merz and F. Houtermans[11].

In the last column is the observed $^{187}Os/^{186}Os$ ratio obtained from mass spectrometric measurements by J. Geiss, B. Hirt, *et al.*[11] in Bern. These ratios show that " radiogenic " ^{187}Os is present in the iron and it might be possible to calculate the age. In all probability we can exclude any interference from cosmic radiation effects. The primordial abundance of the ^{187}Os in the meteorite osmium, however, is still an unknown factor.

Another low natural radioactivity of possible geological interest is that of the ^{176}Lu isotope. In our search for decay products we succeeded in isolating a small amount of pure hafnium oxide in a mineral containing lutetium[12]. After neutron bombardment of hafnium from a Norwegian gadolinite and comparison with an irradiated " normal " hafnium from a zircon mineral it was proved that in the gadolinite hafnium a large part of the ^{176}Hf isotope is present. Normal hafnium is composed of six stable isotopes of which only the isotopes of mass numbers 174, 187 and 180 are suitable for the production of radioisotopes by neutron capture.

In irradiated pure " normal " hafnium we get a certain specific activity of ^{181}Hf, whereas in the presence of a certain amount of stable radiogenic ^{176}Hf, which produces stable ^{177}Hf, the specific activity of ^{181}Hf will decrease proportionally. As in the case of ^{187}Os, here too the difference in specific activity can be used to deduce the amount of " radiogenic " ^{176}Hf present in the sample. The hafnium was isolated in a very pure state from the lutetium mineral by means of ion-exchange techniques. Pile irradiation was carried out for three days with samples containing only 0·05 mg of HfO_2 in a flux of 10^{12} neutrons cm^{-2} sec^{-1}. In order to eliminate interfering activities probably originating from traces of rare earth elements, the

neutron-irradiated HfO_2 samples were dissolved in the presence of lanthanum as hold-back carrier and a relatively high amount of zirconium as carrier. The purification was repeated. Finally the activites were measured under identical conditions by ordinary Geiger–Müller counters or with a γ-spectrometer.

Mass spectrometry proved our results. This work was done by P. Eberhard and P. Signer of the University of Bern with another part of the isolated HfO_2. The results are illustrated in *Figure 5*. The ^{176}Hf isotope is enriched to about 40 per cent in the gadolinite hafnium. It may be noted that the values show good agreement within experimental error.

The hafnium from the gadolinite mineral shows a decrease in the specific activity which is roughly half of the normal standard hafnium. The content in " normal " hafnium can be read directly from the ratio of the specific

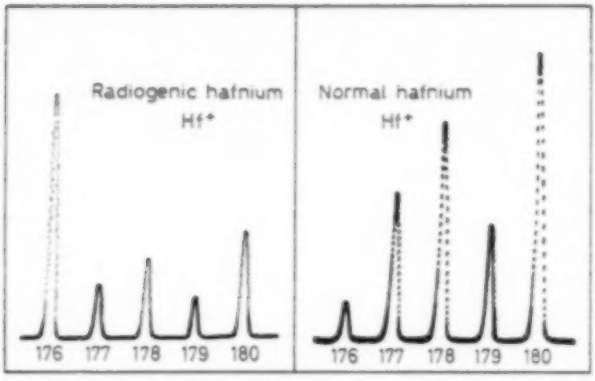

Figure 5. Mass spectrum of hafnium

activities of the unknown sample to that of the hafnium standard. The constancy of the isotopic composition of the " normal " hafnium or standard hafnium can always be ascertained. It is worth mentioning that the radiometric abundance analysis of radiogenic hafnium was also done with the ^{176m}Hf activity ($t_{\frac{1}{2}} = 19$ sec) which has a high thermal neutron cross-section (~ 100 barns). But the gain in time brings a loss of accuracy owing to difficulties in fast handling.

Thus we succeeded in determining the half-life of ^{176}Lu and proved the use of this isotope in geological dating work, especially in minerals containing rare earths and lutetium.

In the introduction I mentioned the importance of reliable uranium determinations in terrestrial and in cosmic matter. Reed and Turkevich[9] have used neutron activation techniques to determine reliable data on the uranium content of meteorites. They had to correct the older iron figures by at least 10^2. This work was started because of remaining discrepancies in the calculation of heat production and stability of planetary bodies. In this work the uranium-fission product ^{140}La was separated from the irradiated samples and simultaneously the yield in ^{239}Np (formed by

Table 6. Uranium contents by neutron activation using ^{133}Xe fission products (from H. König and H. Wänke[13])

Meteorite	$10^8 \times$ U *content* (g/g)	*Meteorite*	$10^8 \times$ U *content* (g/g)
Chondrite		*Achondrite*	
Akaba	$0{\cdot}82 \pm 0{\cdot}05$	Johnstown	$0{\cdot}19 \pm 0{\cdot}06$
Beardsley	$1{\cdot}13 \pm {0{\cdot}11 \atop 0{\cdot}09}$	Nuevo Laredo	12·6*
Beddgelert	$2{\cdot}10 \pm 0{\cdot}19$	Pasamonte	$5{\cdot}40 \pm {0{\cdot}50 \atop 0{\cdot}30}$
Breitscheid	$1{\cdot}23 \pm 0{\cdot}07$	Sioux County	$6{\cdot}30 \pm 0{\cdot}40$
Forest City	1·03*		
Holbrook	1·25*		
Modoc	$1{\cdot}04 \pm {0{\cdot}10 \atop 0{\cdot}06}$		
	1·08*		
Pultusk	$1{\cdot}23 \pm 0{\cdot}10$		
Richardton	1·22*		

* Results from H. Hamaguchi, G. W. Reed and A. Turkevich using neutron fission: $^{235}U(n,f)^{140}Ba$ and $^{238}U(n,\gamma,\beta^-)^{239}Np$.

$^{238}U(n,\gamma)^{239}U \xrightarrow{\beta} {}^{239}Np$) was measured, proving that the isotope composition of uranium in meteorites is normal. The chemical procedure is rather tedious and somewhat time-consuming.

The glass apparatus used for the argon determination is also suitable, after slight modification, for uranium determination, as König and Wänke[13] showed recently. They used the $^{133}Xe(t_{\frac{1}{2}} = 5{\cdot}2\ d)$ fission activity with success. The method is reliable and has many advantages.

In *Table 6* their uranium results in stone meteorites are summarized. Some of the values marked with an asterisk can be compared with results from Reed and co-workers. ^{133}Xe is unaffected by other nuclear reactions. The purification process, absorption on charcoal and desorption at 140°C,

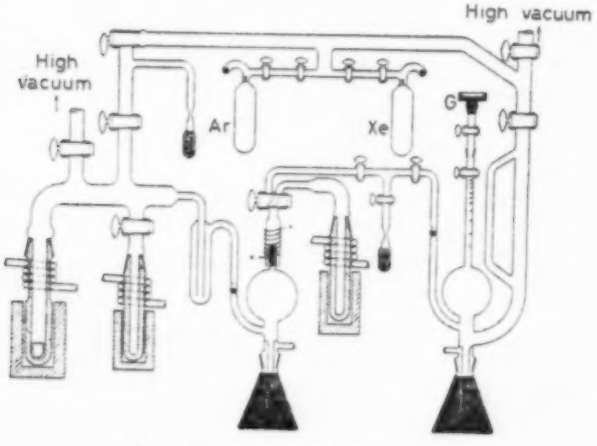

Figure 6. Modified Wänke apparatus

eliminates all other possible interfering gaseous activities. As most of the meteorites are rare and therefore valuable materials it is convenient to make age determinations, uranium analyses, *etc.*, on the same sample.

Figure 6 shows the modified apparatus of Wänke. It is only some years ago that Paneth and co-workers[14] discovered that helium in iron meteorites is a mixture of ^{3}He and ^{4}He. It is considered that helium is produced by cosmic radiation as a spallation product of iron. The ^{3}He/^{4}He ratio is fairly constant at $\sim 0{\cdot}25$. With regard to ^{3}He a precursor, ^{3}H, has to be expected. The first experimental approach made by Begemann, Geiss and Hess[15] proved the existence of tritium in the stone meteorite Norton County, and they calculated from the amount of ^{3}H and ^{3}He a so-called " radiation age " (t_r), *i.e.*, the time needed to produce the ^{3}He found:

$$t_r = \frac{\text{the number of } ^3\text{He atoms (corrected for direct production)}}{\text{the number of } ^3\text{H decays per second}}$$

The radiation age for " Norton County " was found to be in the range of 250 million years on the assumption that the cosmic-ray production was constant over that time. The potassium–argon method gives a greater age, of $\sim 4 \times 10^9$ years.

Fireman and Schwarzer[16] reported on the determination of ^{3}He in meteorites by neutron activation. ^{3}He has a high neutron cross-section of ~ 6000 barns and consequently it is detected with high sensitivity. On the other hand, the ^{3}H in the freshly fallen meteorite can be measured only by low-level counting techniques. The two methods combined give valuable information about the earlier events in our planetary system. We may best understand the " radiation age " as the time in which smaller meteorites were circling in space, not shielded by big masses from interactions with cosmic radiation. In other words, collisions of bigger bodies took place at the beginning of this time.

It is worth mentioning that the same technique for the estimation of ^{3}He by neutron activation is also applicable to the determination of lithium by the ^{6}Li(n,α)^{3}H reaction in meteorites. Lithium is (at least partially) of radiogenic origin. After driving out the ^{3}He from the sample, in a following irradiation only the ^{6}Li(n,α)^{3}H reaction will contribute to the formation of tritium.

In connection with these investigations on cosmic matter, quite recently Wänke[17, 18, 19] discovered that ^{45}Sc (the element consists of one stable isotope) is also produced by cosmic radiation in iron meteorites. The scandium concentration lies in the region of 10^{-9} g/g of iron. Relative to the helium and neon contents he found that the scandium content is nearly proportional to the contents of these gases. These results are given in *Table 7*.

It is found that only a small part (*ca* 10 per cent) of scandium is not of cosmogenic origin. It is indeed remarkable that meteorites with very small amounts of helium also show a very small scandium concentration. From these figures the conclusion can be drawn that cosmogenic helium was never lost by a possible intermediate heating, a possibility which was discussed earlier by several scientists.

Table 7. Scandium contents of iron meteorites compared with helium and neon contents
(from H. Wänke—to be published)

Meteorite	*Weight* (kg)	$10^6 \times$ He *content* (cm^3/g)	$10^8 \times$ Ne *content* (cm^3/g)	$10^9 \times$ Sc *content* (g/g)	*Ratio* He/Ne	*Ratio* $\frac{Sc - 0{\cdot}2 \times 10^{-9}}{Ne}$
Savik	66,000	<0·0002	—	0·14	—	—
Muonional	7·5	<0·002	—	0·2	—	—
Gibeon (Harvard)	15,000	0·36	—	0·2	—	—
Odessa	large	—	—	0·35	—	—
Gibeon (Amalia)	15,000	3·51	1·98	0·40	177	5
Bendego	5360	7·62	4·70	1·1	162	9
Carbo	450	21·2	12·9	1·9	167	6·5
Tamarugal	320	23·1	14·7	2·2	157	6·6
Treysa	63	25·4	19·1	2·1	133	4·9
Thunda	60	27·1	18·7	2·6	145	6·4
Mt Ayliff	14	36·2	26·7	3·6	136	6·5
Clark County	11·3	44·0	33·6	4·7	131	6·6

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Further, the following conclusion was made. If the energy of all primary cosmic ray particles lies above 10^9 eV, and the generally assumed energy spectrum for the range 10^9 eV to 15×10^9 eV is correct, the ratio of Sc/Ne should be 1·4. However, even in small meteorites, where spallation reactions induced by low-energy secondary particles are of little influence, the ratio found was about 6·5. From this it is concluded that the primary component of the cosmic radiation contains a relatively high percentage of particles with energies below $1{\cdot}0 \times 10^9$ eV, so the "cut-off" in the range $< 1 \times 10^9$ eV should not exist. The "cut-off" is only effected by the influence of the magnetic field of the earth and the flux of the primary radiation has to be two or three times higher than that measured by rocket and balloon experiments. To understand these conclusions it is necessary to mention that scandium is a special case insofar as its spallation cross-section in iron by protons energies higher than 350 MeV is fairly constant. This is not the case for neon where the cross-section rises sharply with the energy of the incident protons.

Many other applications in the wide field of geochemistry could have been mentioned. The results of radioactivation analysis should shed light on such problems as the cosmic abundance of elements, the distribution relationship of trace elements in different phases, the radioactive balance of mother and daughter substances, *etc.* An important problem still will remain the study of the course of nucleogenesis, especially of the higher elements.

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DISCUSSION

G. W. Reed (*U.S.A.*): I should like to discuss some work performed at the Argonne National Laboratory and at the University of Chicago in which activation analysis has been used to determine isotopic compositions of elements present in amounts ranging from 10^{-6} to 10^{-9} g/g. The participants in this work other than myself and Professor Anthony Turkevich (University of Chicago) were Professors H. Hamaguchi and K. Kigoshi of Japan.

I should like to re-emphasize first the versatility of the method. Extremely small quantities, isotope ratios, a large number of elements in the same sample and irradiation, fast as well as slow neutron reactions, freedom from accidental contamination—no prior separations are necessary—are all factors which make this an attractive and, frequently, the only method for doing reliable analyses.

In reply to the physicists I should like to point out that frequently one is measuring a few counts in samples initially having curie levels of activity and it seems unlikely that the chemist can be dispensed with. The experimental results shown were really secondary, except for lead, to the purpose of the experiments which was to measure concentrations.

Table 8 indicates the sensitivity of the method. As Dr Cook has already pointed out, the two really important factors are the half-life and cross-section. The sensitivities in the last column are based on these values and

Table 8. Nuclear data and sensitivity

Nuclide and reaction	*Cross-section of isotope for thermal neutrons* (barns)	*Half-life of product nuclide*	*Approximate sensitivity* (μg)
$^{238}U(n,\gamma,\beta^-)^{239}Np$	2·8	2·33 d	10^{-6}
$^{235}U(n,f)^{140}Ba$	4·2	12·8 d	5×10^{-5}
$^{232}Th(n,\gamma,\beta^-)^{233}Pa$	7	27·4 d	3×10^{-6}
$^{209}Bi(n,\gamma)^{210}Bi$	0·019	5·0 d	3×10^{-4}
$^{208}Pb(n,\gamma)^{209}Pb$	0·00045	3·3 h	1
$^{204}Pb(n,2n)^{203}Pb$	$(0{\cdot}002)_{eff}$	52 h	1
$^{203}Tl(n,\gamma)^{204}Tl$	11	4·1 y	2×10^{-4}
$^{202}Hg(n,\gamma)^{203}Hg$	3	46·9 d	3×10^{-5}
$^{196}Hg(n,\gamma)^{197}Hg$	2500	65 h	6×10^{-7}

Table 9. Terrestrial rocks

Type		*Heavy elements* (μg/g)			
		Pb*	Bi	Tl†	U*
Perthite (Tory Hill)	Activation analysis	6·7 ± 0·2	0·011	2·3	0·3
	Literature	9·5		3·1	0·34
Basalt (Snake River)	Activation analysis	6·8 ± 0·2	0·0076	0·073	0·84
	Literature	6·5		0·124	0·8

* From G. R. Tilton *et al.* *Bull. Geol. Soc. Am.*, **66**, 1131 (1955) and C. Patterson, G. R. Tilton and M. Inghram. *Science*, **121**, 69 (1955).
† Averages of several granites and four basalts from D. M. Shaw. *Geochim. et Cosmochim. Acta*, **2**, 118 (1952).

activity measurements made 18 h after a three-day irradiation at a flux of about 10^{13} neutrons cm^{-2} sec^{-1}.

Table 9 gives a comparison of our results with measurements made by other methods. The samples were not the same, hence the differences are not surprising. It is obvious that for the relatively large quantities measured the results are in good agreement.

All the results are based on comparison measurements, thus avoiding absolute flux, disintegration rate, half-life and cross-section determinations.

In the data that follow I should like to point out that we were dealing with about 10^{-6} g of barium, 10^{-9}–10^{-5} g of mercury, 10^{-6}–10^{-5} g of lead, and 10^{-8}–10^{-7} g of uranium.

^{130}Ba and ^{134}Ba in meteorites have been determined and the results are given in *Table 10*. The barium measurements were made on electrons

Table 10. Isotopic composition of meteoritic barium

Meteorite	$\frac{(^{135}Ba/^{131}Ba)\ meteorite}{(^{135}Ba/^{131}Ba)\ monitor}$
Modoc	1·08
	1·00
Holbrook	1·02
Beardsley	0·98
Indarch	0·97
Nuevo Laredo	1·08
Average	1·03 ± 0·05

arising, in the case of 29-hour ^{135}Ba, from conversion of the gammas associated with the decay of the excited state and, in the case of ^{131}Ba, from conversion of the gammas arising from 11·6-day orbital electron capture. The measurements were, of course, quite sensitive to sample thickness and the data quoted are from samples and monitors of nearly the same weight. Within 5 per cent the isotopic ratio of these two is the same as for terrestrial barium. The 5 per cent is the uncertainty in the average and could undoubtedly be improved upon in experiments in which such a measurement is the primary purpose. This holds for the results for uranium in *Table 11* and also for mercury.

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Table 11. Uranium contents of meteorites*

Meteorite	$10^6 \times$ U *content* (g/g)	
	via ^{239}Np	*via* Ba–^{140}La
Chondrites:		
Forest City	(1·30)	0·97
	1·05	1·11 ± 0·18
	0·92	1·15
Average	0·99	1·06
Modoc	1·08	1·08
Richardton	1·31	1·15 ± 0·14
	1·14 ± 0·33	1·05 ± 0·26
Average	1·30	1·13
Holbrook	1·54 ± 0·25	1·17 ± 0·24
	1·36	1·11 ± 0·18
Average	1·40	1·12
Achondrite:		
Nuevo Laredo	12·5	12·5
	12·0	10·8
	13·2	14·0
Average	12·6	12·6
Minerals:		
Hualalai Basalt	46·3	45·2
Twin Cities Dunite	0·10	0·14 ± 0·07
	0·10 ± 0·08	0·11 ± 0·05
Average	0·10	0·12

* H. Hamaguchi, G. W. Reed and A. Turkevich. *Geochim. et Cosmochim. Acta*, **12**, 337 (1957).

The ^{235}U and ^{238}U measurements involved preparing different samples in contrast to all the other measurements. One was for neptunium and the others were for barium and lanthanum. In spite of this the meteoritic and terrestrial uranium is shown to have the same isotopic composition to within 10 per cent. Neptunium was measured as a weightless sample from a fixed position in the counter to avoid the complications arising from the large number of low energy betas. Barium and lanthanum have sufficiently hard radiations so that their measurement is not difficult.

Data on the isotopic ratio ^{196}Hg/^{202}Hg are shown in *Table 12*. Weak radiations also make the mercury measurements difficult. It was necessary here, as with all nuclides measured, to prepare scattering and absorption

Table 12. Isotopic composition of mercury in meteorites

Meteorite	^{196}Hg/^{202}Hg *in meteorite vs monitor*
Canyon Diablo Troilite	1·02
Toluca Troilite	1·06
Nuevo Laredo	1·02
Orguiel	0·92
	1·01 ± 0·06

vs sample weight curves. ^{197}Hg decays by electron capture and is particularly sensitive to variations in sample thickness and counting position. The 0·92 value for the last sample arises from the fact that the sample was too "hot" to measure under our standard counting conditions and corrections had to be made.

D. MAPPER (*U.K.*): I think Dr Herr would agree that although he has dealt with the use of activation techniques in age determinations, the method of isotope dilution, *e.g.*, in rubidium–strontium age determination in stone meteorites, is, generally speaking, the best technique to employ. It is in regard to abundance determinations that neutron activation analysis is of the greatest importance. Results on meteorites and rocks illustrating both approaches have recently been published*. The great advantage of activation analysis is that a large number of elements can be determined on small quantities of sample with complete freedom from the blank and contamination difficulties which are so common in other methods of trace analysis. Activation analysis is now playing a major role in geochemical abundance determinations.

W. W. MEINKE (*U.S.A.*): I should like to describe some work on the radioactivation analysis of meteorites and other materials carried out at the University of Michigan. The facilities of the reactor and hot laboratory of the Michigan Memorial Phoenix Project have been modified to allow measurements on radioisotopes of short half-life.

By means of pneumatic tubes it is possible to bring a sample from the core of the reactor directly into the hood in the neighbouring chemistry laboratory, while an auxiliary tube system carries a prepared counting sample down to the detector for rapid measurement†. A special 100-channel pulse-height analyser with two memories has been constructed for use with radioisotopes of short half-life. One memory is plotted while the other is stored and then, on a given signal, the two memories are switched. Samples can be taken from the reactor to the counting equipment in a total of five seconds plus transfer time and/or radiochemical separation.

The graph obtained when calculated sensitivity values‡ at a flux of 10^{12} neutrons cm^{-2} sec^{-1} for a six-minute irradiation are plotted against the half-lives, and similar graphs for irradiation times of ten and one thousand hours have been published§. Some isotopes with a very high sensitivity, such as rhodium, silver, vanadium, *etc.*, are ideal for radioactivation analysis if a fast radiochemical procedure is developed.

Rhodium, silver and indium have been studied in amounts of 0·1 parts/million in meteorites‖. The key to the work on meteorites is the technique, developed by Schindewolf and Wahlgren, of dissolving the finely divided meteorite sample in about 1½ min by fusion with sodium peroxide in a nickel crucible and then dissolving that solution in hydrochloric acid. Radiochemical procedures have been developed which require only nine minutes for the rhodium and five minutes for the silver determinations.

* A. A. Smales *et al.* "Some geochemical determinations using radioactive and stable isotopes", *Proc. U.N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958*, **2**, 242 (1958).
† These facilities are described in *Nucleonics*, **17**, No. 9, 86 (1959).
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The work on the determination of vanadium in samples of oil is similar to that reported by Dr Colard at the first meeting of this Symposium*. J. Brownlee has worked on the determination of vanadium in samples of oil and cracking catalysts. The results have been reported at the Boston meeting of the American Chemical Society in April 1959 and will be published by *Analytical Chemistry*.

Difficulties are encountered if a cracking catalyst has to be analysed instead of a crude oil sample—a point of considerable importance in the oil industry. The best method of overcoming the difficulties is to treat the cracking catalyst by the same sort of procedure as that used for meteorites. A separation of the vanadium can be made in about ten minutes, and sensitivities in the order of 0·01 μg can be obtained.

On the whole, analysis on vanadium can be made within two or three half-lives of the 3½-minute vanadium.

L. Gorski (*Poland*): It is possible to use the technique of radioactivation analysis in geological wells, but the problems involved are different from those which arise when using a reactor. The concentration of the elements sought is much greater, but the neutron sources are much weaker. We have employed several Po–Be sources or else special neutron generators operating on the T + D reaction. The advantages are considerable. Results are obtained very quickly, and are representative for a wider area than the actual diameter of the well. The method could be employed in prospecting for ores containing copper, vanadium, molybdenum and other metals.

* See p. 30.

L'ANALYSE PAR RADIOACTIVATION AU SERVICE DE L'INDUSTRIE

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A main feature of activation analysis is its extreme sensitivity. Hence it has been principally employed for trace detection and its most extensive use has been in the control of semi-conductors and very pure metals. The need to activate the samples in an atomic reactor has, however, hindered its systematic utilization. The errors inherent in radioactivity measurements make it little suited for determining the main constituents of a sample. On the other hand, the utilization of radiation-matter interactions seems to open the way to a whole series of non-destructive and rapid analyses which are worthy of note, although they are not, strictly speaking, activation analyses.

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Lorsque l'Agence Internationale de l'Energie Atomique m'a demandé de faire un exposé sur l'analyse par radioactivation au service de l'industrie, je me suis trouvé fort embarrassé pour délimiter mon sujet. En effet, le Dr C. W. Leddicotte devait traiter de l'analyse par radioactivation aux Etats-Unis et connaissant personnellement l'auteur, je savais qu'il donnerait de nombreux exemples empruntés à l'industrie et d'autre part le Dr J. Hoste devait traiter de l'analyse par activation en métallurgie. Afin d'éviter les doubles emplois, je vais essayer de vous montrer quelle est la place de l'analyse par activation parmi les autres méthodes d'analyse. De plus, je pense que le terme d'analyse par activation devient trop étroit et qu'il faudrait plutôt parler des radioéléments au service de l'analyse. Dans cet ordre d'idée, je crois que l'utilisation des propriétés du rayonnement permet d'envisager le développement de nouvelles méthodes d'analyse.

COMPARAISON AVEC LES AUTRES MÉTHODES D'ANALYSE

Comme le dit le Dr G. B. Cook dans son exposé, ce qui caractérise l'analyse par activation est son extrême sensibilité, variable évidemment suivant les éléments. L'analyse par activation trouve donc un emploi privilégié partout où il s'agit *de détecter des traces*. En effet, les méthodes chimiques classiques seraient bien incapables de doser certaines terres rares (Dy, Eu, Sm) dans le graphite[1] à des teneurs de 10^{-9} g/g, ou les contaminants des semi-conducteurs à des teneurs du même ordre de grandeur[2] ou enfin les contaminants de métaux très purs[3]. Les autres méthodes physico-chimiques: polarographie, colorimétrie, ou physiques: spectrographie d'émission, ont des sensibilités moindres. De plus, dès qu'il y a mise en solution, les risques de perte par adsorption, par coprécipitation, deviennent très grands et les résultats n'ont plus de sens. Le fait qu'après activation il soit possible d'ajouter la quantité d'entraîneur que l'on veut, permet de faire toutes

les séparations chimiques sans danger. Cependant, il s'agit le plupart du temps d'activer le matériau dans un réacteur nucléaire, ce qui freine un peu le développement de la méthode. Bien sûr, il existe d'autres modes d'activation tels que les accélérateurs et les sources de neutrons (Ra + Be par exemple), mais les flux dont on dispose sont moindres. On perd en effet un facteur 10^3 en passant d'un réacteur moyen à un Van de Graaff et d'un facteur 10^8 en utilisant une source de Ra + Be de 1 curie. Notons en passant qu'une telle source vaut 100.000 nouveaux francs français, ce qui décourage d'éventuels utilisateurs. Les sources polonium–béryllium sont plus accessibles et nécessitent une plus petite protection gamma, mais la demi vie trop courte du polonium amène un remplacement périodique des sources. Evidemment, les appareils peuvent être utilisés comme sources de particules chargées ou comme sources de photons énergiques, ce qui permet d'étendre l'analyse par activation aux éléments légers. Je citerai par exemple le dosage du bore dans le germanium.[4]

L'analyse par activation est accompagnée d'un certain nombre d'erreurs inhérentes à la méthode, si bien que la précision globale de la détermination ne dépasse que rarement le un pour cent fatidique. Dans certains cas de déterminations de faibles traces, il faut parler le plus souvent de 10 pour cent. Dans ces conditions, la méthode devient moins intéressante pour la détermination des constituants principaux d'un échantillon. Les autres méthodes sont concurrentielles. Cependant, l'analyse par activation peut apporter un gain de temps important dans tous les cas où la mise en solution est longue. C'est ainsi que nous avons déterminé le fluor et le chlore dans des trifluorochloroéthylènes. Il faut citer aussi le dosage de certains constituants des verres[5]. D'autre part, l'analyse par activation peut rendre de grands services dans tous les cas où les séparations chimiques sont difficiles ou incomplètes.

L'INTÉRACTION RAYONNEMENT MATIÈRE COMME MOYEN D'ANALYSE

Un des obstacles au développement de l'analyse par activation est, nous l'avons déjà vu, la nécessité de posséder un moyen puissant d'activation. On ne se procure pas un réacteur atomique ou un Van de Graaff comme on se procure un spectrographe à réseau! Par contre, il est possible d'acheter des radioéléments à longue période et d'utiliser leur rayonnement. Je voudrais faire un inventaire aussi complet que possible de nos moyens actuels.

Méthodes par absorption

Le propre de cette méthode est de mesurer l'affaiblissement d'un faisceau de rayonnement ou de particules. On peut citer de nombreux exemples. Les plus anciens peut-être furent ceux de l'industrie du pétrole:

dosage du soufre dans les pétroles bruts[6] par absorption de la raie X de 6 keV émise par le fer-55; plus récemment, cette source a été remplacée par une source de rayonnement de freinage: tritium adsorbé sur titane[7];

dosage du plomb tétraéthyle dans l'essence par absorption du rayonnement de freinage d'une source de tungstate de prométhéum[8];

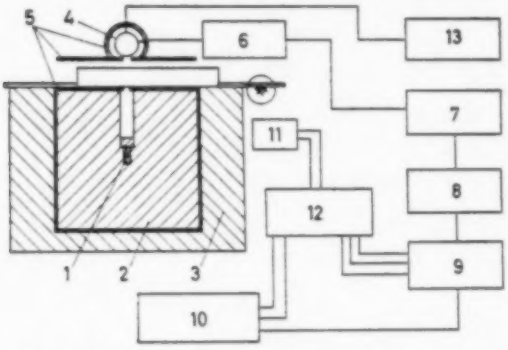

Figure 1. Dispositif pour la mesure d'humidité par absorption de neutrons thermiques: 1 source de neutrons; 2 parafine; 3 plomb; 4 détecteur de neutrons lents; 5 cadmium; 6 préamplificateur; 7 amplificateur; 8 discriminateur d'amplitude; 9 échelle de comptage; 10 enregistreur automatique; 11 moteur; 12 programmateur; 13 haute tension

mesure du rapport C/H par l'analyse fine de l'absorption du rayonnement bêta[9].

Mais on peut utiliser aussi l'absorption des neutrons thermiques. La *Figure 1* montre le dispositif utilisé dans ce cas. Les neutrons thermiques sont produits par un classique " canon à neutrons ". Le relevé des résultats numériques est fait automatiquement.

La *Figure 2* est un exemple de l'utilisation de cette méthode pour le dosage de l'humidité dans des produits divers[10]. Nous avons pu mettre en évidence la diffusion de l'eau d'un sable humide vers un sable sec. On a aussi utilisé cette méthode pour le dosage du bore dans le pyrex[5].

Il suffit alors d'utiliser des sources de (Ra + Be) de quelques millicuries seulement.

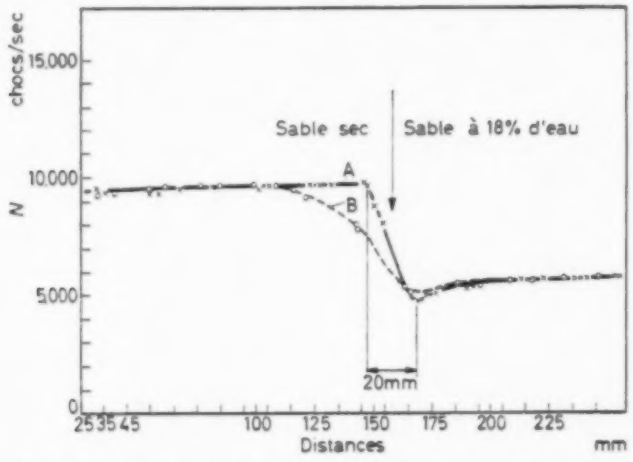

Figure 2. Diffusion de l'eau dans le sable: A, exploration automatique d'un échantillon mixte immediatement après sa préparation; B, exploration automatique du même échantillon 3 h après sa préparation

Méthode par diffusion

L'étude systématique de la rétrodiffusion du rayonnement bêta a permis de mettre au point un certain nombre d'analyses non destructives. On utilise dans tous les cas le fait que la rétrodiffusion des électrons est proportionnelle à $Z^{\frac{1}{2}}$. On peut citer:

le dosage du tungstène dans les aciers[11];

l'analyse de solutions binaires[12, 13].

Sous cette rubrique il faut rappeler le dosage de l'humidité par thermalisation de neutrons rapides.

Méthode par excitation

On peut exciter les raies X caractéristiques d'un élément soit par des électrons provenant d'une source bêta[14, 15], soit par les raies X émises par certains radioéléments[16] qui décroissent par capture *K*. Sur la *Figure 3* on peut voir la raie X caractéristique du plomb. Les raies X des autres éléments sont en dessous du seuil de l'appareil. L'utilisation d'un compteur proportionnel à remplissage krypton ou argon, ou d'un photomultiplicateur d'électrons associé à un cristal mince permet de sélectionner les énergies X voulues et d'obtenir aussi des analyses rapides. Cette méthode est en cours d'exploration au Commissariat à l'Energie Atomique et déjà nous avons mis au point, en collaboration avec l'Institut de Recherches Sidérurgiques, le dosage du fer et du calcium dans les minerais de fer[17]. Pour cette application, nous avons réalisé un ensemble représenté par la *Figure 4*. L'aimant permanent nous permet d'éliminer les électrons rétrodiffusés qui donneraient un bruit de fond trop élevé.

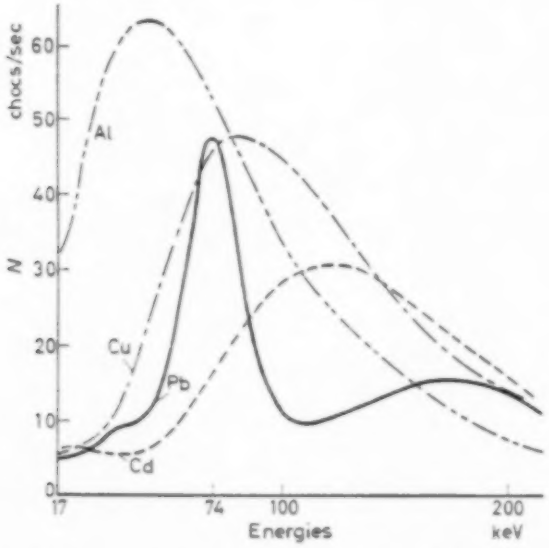

Figure 3. Spectres de bremsstrahlung de ^{90}(Sr + Y) (β^- de 2·18 MeV) transmis par des cibles de 1 g/cm^2

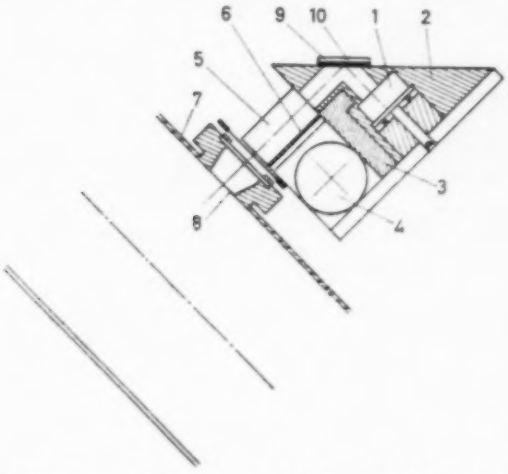

Figure 4. Tête de mesure pour la fluorescence β.X: 1, source β (^{90}Sr + ^{90}Y); 2, corps en aluminium; 3, bouclier en plomb; 4, aimant permanent; 5, entrefer; 6, écran en Plexiglass; 7, compteur proportionnel; 8, beryllium: 20 mg/cm^2; 9, support; 10, depôt

On peut classer également dans cette catégorie le dosage isotopique du lithium. Le sel à analyser est mélangé à du sulfure de zinc et le tout est irradié par les neutrons thermiques provenant d'une source (Ra + Be) noyée dans la parafine. Un photomultiplicateur détecte les éclairs émis par le sulfure de zinc lorsque les produits de la réaction ^{6}Li(n,α)^{3}H heurtent une particule de ZnS.

Rappelons également le dosage du bore dans les aciers[18] par réaction (n,α) et détection de ceux-ci par plaques photographiques.

Comme on le voit, l'utilisation des propriétés du rayonnement amène toute une gamme variée d'analyses qu'il est difficile d'appeler par activation et qui pourtant font appel à des radioéléments.

Pour être complet il faudrait signaler également tous les services qu'a pu rendre à l'analyse l'emploi des radioéléments pour la mise au point de méthodes et pour l'étude de la chromatographie. Ce bel ensemble de réalisations montre combien le développement de l'énergie atomique a été bénéfique à l'analyse.

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DISCUSSION

J. Hoste (*Belgium*): In connection with radioactivation analysis involving particles other than neutrons, we have used 12 MeV deuterons at the University of Ghent to determine magnesium in nodular cast iron in amounts of 0·1–0·01 per cent. As it is difficult to monitor deuterons produced in a cyclotron precisely, an internal standard has been used. The magnesium produced sodium-22 by the (d,α) reaction, the reaction for the internal standard being ^{56}Fe(d,α)^{54}Mn. Sodium-22 is a long-lived isotope, which is essential as the cyclotron at Louvain is more than 50 miles away from Ghent. After irradiation, the target is dissolved in strong hydrochloric acid, the iron extracted with isoamyl acetate and the aqueous solution passed through an anion-exchange column to separate the sodium-22 from the manganese-54. From the ratio of the activities of ^{22}Na and ^{54}Mn a calibration curve can be constructed. When ten minute irradiations are used with a beam strength of 100 μA, it is possible to measure down to 0·01 per cent of magnesium in nodular cast iron.

G. B. Cook (*U.K.*): I should like to add a few comments on the subject of X-ray fluorescent spectroscopy which has some interesting applications to analysis in industry.

Where a β-source such as ^{35}S is used to excite the target, the bremsstrahlung produced has a wide energy range with non-characteristic interactions with the target, for instance the Compton effect. Much lower background effects are obtained if the β-sources are replaced by K-capture isotopes, where only monoenergetic photons are concerned. With a barium target, for example, a characteristic barium curve with a sharp peak and very little background is obtained.

If a proportional counter is used to distinguish the energies of the induced X-radiation, the essential requirements of X-ray fluorescent spectrometry are met. Although the resolution of the proportional counter is not as high as that of an instrument using an X-ray tube and crystal spectrometer, it is sufficient to permit separation of elements differing in atomic number by three or more, but it is difficult to separate elements differing in atomic number by two, and impossible if they differ by only one.

While this technique is not sufficiently sensitive for the detection of trace elements, it is adequate for the purposes of many simple analyses and has many industrial applications, such as measuring the thickness of a layer of chromium-plating on nickel down to 10^{-6} in., or rapidly distinguishing various types of steel in factory stocks by measuring the molybdenum content, which we have determined down to 0·1 per cent in a series of specimens.

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This result was equal to those obtained by a non-dispersive system with an X-ray tube as exciter and a proportional counter for energy resolution; at the same time, the background/signal ratio was better in the *K*-capture isotope system because only a single energy-line was measured.

The use of this technique is somewhat restricted by the difficulty in obtaining suitable exciter sources. ^{131}Cs (with a rather short half-life of 10 days), ^{55}Fe, ^{241}Am and some others have been used. On the other hand, 100 μc of active material is usually enough for a source.

This work has been performed by C. E. Mellish and J. A. Payne of the Isotope Division at Harwell.

D. MAPPER (*U.K.*): Since Dr Leveque has mentioned methods of analysis other than neutron activation, I should like to mention an example of proton activation analysis carried out by R. A. Gill in the Analytical Chemistry Group, Harwell*. A method is described of determining boron in silicon in quantities down to 10^{-9} g by proton activation analysis. The method is of importance in semi-conductor work.

Samples were irradiated in the synchro-cyclotron at Harwell with protons of a maximum energy of 20 MeV. The principal reactions were $^{11}B(p,n)^{11}C$, a positron-emitter with a half-life of 20·4 min, and $^{30}Si(p,n)^{30}P$, also a positron-emitter with a half-life of 2·5 min. The ^{11}C was chemically separated from the silicon in the presence of carrier and the ratio of the activities of ^{11}C and ^{30}P was determined.

E. SOMER (*Denmark*): Has activation analysis been used in France for the determination of poisonous trace elements in wines and spirits, *e.g.*, arsenic, zinc, copper and mercury, which may be introduced by the use of pesticides in the growing of the grapes? In many countries there are strict regulations on the maximum permissible amounts of these elements in foodstuffs. We have found that activation analysis is important in this field.

We have developed a systematic analysis for the determination of arsenic, zinc and copper in vegetables, fruit juices and cherry brandy.

Samples and standards are irradiated at a flux of 10^{12} neutrons cm^{-2} sec^{-1} for 1–3 days. After addition of arsenic, copper and zinc carrier, organic matter in the sample is destroyed by treatment with fuming nitric acid and concentrated sulphuric acid. The sample is evaporated with hydrochloric acid and is made 0·4N with regard to hydrochloric acid after neutralization with sodium carbonate. Sulphides are then precipitated with hydrogen sulphide. The washed precipitate is dissolved in aqua regia. After neutralization sodium sulphide is added and copper is determined in the precipitate. Sulphuric acid is added to the filtrate and arsenic is determined in the precipitate. Hydrogen sulphide is removed from the filtrate of the hydrogen sulphide precipitation and sodium hydroxide and sodium peroxide are added. The solution is kept at 80°C for 15 min and centrifuged. Sodium sulphide is added to the filtrate and zinc is determined in the precipitate.

* R. A. Gill. "Proton activation analysis in the determination of sub-microgram amounts of boron in silicon", *A.E.R.E. Report* No. C/R 2758, 1958.

The activity of the precipitates is measured in a gamma spectrometer to ensure radiochemical purity or to discriminate against activities from other elements.

The concentrations usually found are 0·1–5 parts/million and the accuracy is better than 20 per cent.

M. Leveque mentioned that only tritium bremsstrahlung sources had been used in the oil industry for the determination of sulphur and lead. We have used these sources in the paper industry in thickness gauges for the measurement of P.V.C. and Saran coatings on paper (water-vapour-tight paper). Owing to the chlorine content of the coating the radiation is absorbed more strongly in the coating than in the paper. The absorption in 1 mg/cm² Saran is the same as in 5 mg/cm² of paper and the method is thus insensible against variations in the paper thickness.

P. LEVEQUE (*France*): I have had no experience in determining trace elements in wine.

J. M. A. LENIHAN (*U.K.*): The possibility of arsenic contamination of wine is not to be lightly dismissed. In the early years of this century a serious outbreak of arsenical poisoning among beer-drinkers in the United Kingdom was investigated under Lord Kelvin and found to be due to arsenic introduced into the beer with glucose in the manufacture of which impure sulphuric acid was used.

Quite recently, a number of hair samples provided by female laboratory workers were found to be rich in arsenic, the origin of which was traced to the laboratory detergent which they sometimes used to wash their hair. The two widely used synthetic detergents concerned were found to contain up to 100 parts/million of arsenic. They were produced from shale oil by means of sulphuric acid made from pyrites by the lead chamber process. In spite of the additional cost, the manufacturers concerned now use arsenic-free sulphuric acid.

H. SELIGMAN (*I.A.E.A.*): Machine analysis presents a difficult problem in that the need to heat the target may affect the target material.

G. W. LEDDICOTTE (*U.S.A.*): Our laboratory has not yet been approached by the wine industry but we have done much work of a similar kind, such as the analysis of yeasts, the localization of various trace substances in sugar cane, testing for the presence of selenium in cattle food (which is important in areas where cattle suffer from white mitosis), and the analysis of vitamin products originating in cereals. In the last case our laboratory has been able to make a semi-quantitative analysis of about seventy substances in hay. Many problems of this general nature can best be solved by radioactivation analysis.

J. GILAT (*Israel*): Dr Steiger of the Technion in Haifa reported at the Second United Nations International Conference on the Peaceful Uses of Atomic Energy on a method of gauging the thickness of histological and other biological specimens by using the absorption of α-particles from polonium. It was also possible to calculate the elemental composition at various points on the samples and its variation.

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EXPERIENCE IN THE U.S.A. ON THE USE OF RADIOACTIVATION ANALYSIS

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Aux Etats-Unis, de nombreux chercheurs dans diverses branches de la science se servent maintenant de la radioactivation qu'ils considèrent comme un outil utile et commode aux fins d'analyse élémentaire. Leurs travaux ont consisté surtout jusqu'à présent à déterminer des concentrations de l'ordre du microgramme ou des concentrations encore plus faibles, d'éléments divers contenus dans des échantillons de substances biologiques, de produits pharmaceutiques, d'engrais, de substances chimiques fines, de produits alimentaires, de carburants, de verre, de matières céramiques, de métaux, de minéraux, de peintures, de dérivés du pétrole, de résines, de sols, de substances toxiques, d'eau et d'autres matières.

Il existe de nombreux types de sources neutroniques, mais la plupart des analyses faites au cours de ces recherches l'ont été au moyen de réactions neutroniques produites soit par une source de faible intensité, soit par un accélérateur, soit dans un réacteur. Dans certains laboratoires et notamment au Laboratoire national d'Oak Ridge, on se sert de l'analyse par radioactivation neutronique de façon presque courante. Le Service des analyses par activation de la Division des analyses chimiques du laboratoire a résolu des problèmes d'analyse nombreux et difficiles au moyen des flux neutroniques produits dans les réacteurs d'Oak Ridge.

Le mémoire a pour objet d'exposer les connaissances que les chercheurs des Etats-Unis ont acquises en employant cette technique. Il est consacré en partie à l'emploi, presque courant, de l'activation neutronique dans le cadre du programme d'Oak Ridge et donne des détails sur la façon dont d'autres chercheurs ont appliqué cette méthode à l'étude de problèmes spéciaux. Dans chaque cas, l'auteur indique par quels moyens les substances étudiées ont été irradiées et comment les substances irradiées ont été ensuite traitées. En outre, il décrit des procédés d'essai sans altération des matériaux et de séparation radiochimique ainsi que les méthodes et l'appareillage utilisés dans la métrologie des radionuclides. Dans tous les cas, il indique le degré de précision de la mesure pour chaque application.

Radioactivation analysis has become a well-established analytical method in the United States of America, and is being used on an increasing scale by many American researchers in analysis problems requiring a most sensitive and specific technique. This paper cites in a cursory way the applications that this method is finding in many different analytical problems. Significantly, most of these applications have been concerned with problems in elemental microanalysis; however, applications in macroanalysis and isotopic analysis have also been made. In addition, radioactivation analysis has been used as a complementary method to other analytical techniques employed in analysis problems of elemental segregation and diffusion, and in the determination of particle-size distributions.

THEORY

Excellent discussions of the overall theory of radioactivation analysis are available[1-3]. The basic principles might be briefly stated by indicating that a sample, when placed in a nuclear particle source, is subjected to a bombardment, or irradiated, by the nuclear particles of that source so that

the element or elements to be determined are transformed into unstable isotopes or radioactive nuclides. Each radionuclide decays with a particular mode of decay and radioactive emission and by virtue of these characteristics it may be detected. A measurement of the radioactivity of a nuclide by applying counting procedures, usually, but not always, after suitable chemical separation, is then a measure of the mass of the stable isotope(s) of the element present in the sample being analysed. The characterization or identification of the radionuclide chosen to complete an analysis is made by examining its nuclear radiations and half-life by some type of counting method.

Most research workers find it practical to irradiate and process simultaneously both the sample being analysed and a weighed standard of the desired element or elements. This practice has minimized such problems as those concerned with an accurate measurement of the nuclear particle flux and the determination of the absolute disintegration rate of the observed radioactivity. Boyd's[1] formula is most generally applied to obtain the concentration of the element being determined:

$$\frac{\text{activity of unknown}}{\text{weight of unknown}} = \frac{\text{activity of standard}}{\text{weight of standard}}$$

Here, a relative counting of the radioactivity in the standard and unknown samples is made. The standard and unknown are usually counted in sequence and under similar counting conditions. After corrections for weight and radioactive decay in each sample, a direct comparison of their radioactivities can be used to measure the element concentration.

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ADVANTAGES AND LIMITATIONS OF THE RADIOACTIVATION ANALYSIS METHODS

Although radioactivation analysis may be used to estimate qualitatively and quantitatively the concentration of a major elemental constituent in a sample matrix, it has been most often used as a microanalytical method. In this area, most of the American researchers using radioactivation analysis methods have done so because the trace element concentrations were beyond detection by other analytical methods. Radioactivation analysis, particularly with neutrons, generally possesses limits of measurement that are potentially more sensitive than those that can be obtained by other analysis methods. *Table 1* gives Morrison's comparison[4] of the limits of measurement for various analytical chemistry methods.

Table 1. A comparison of the limits of measurement of various methods of trace element analysis[4]

Method	*Limits of measurement* (%)
Gravimetric	10^{-2}
Volumetric	10^{-2}
Colorimetric	$\sim 10^{-4}$
Spectrographic	$\sim 10^{-5}$
Mass spectrographic	$\sim 10^{-5}$
Radioactivation	10^{-8}–10^{-10}

Table 2. Quantitative determination of trace elements in metals and alloys by neutron radioactivation analysis

	*Smallest concentration determined** (parts/million)	*Limit of measurement* (parts/million)† *at neutron flux* 5×10^{11}	10^{12}	*Limits of measurement* (parts/million) *by other methods*[6] *Copper spark*	*Flame spectrometer*	*Colour reaction*	*Amperometric titration*
Sb	0·4	0·004	0·0002	5		0·03	10
As	0·1	0·002	0·0001	5		0·1	0·4
Ca	5	4	0·2	0·1	0·03		100
Cd	1	0·05	0·003	2	20	0·01	5
Cs	0·1	0·03	0·002	0·5	1		
Cl	2	0·03	0·002				10
Cr	1	0·2	0·01	0·05	1	0·02	1
Co	0·05	0·02	0·001	0·5	10	0·03	100
Cu	1	0·007	0·004	0·2	0·1	0·03	10
Ga	13	0·007	0·0004	1	1		
Au	0·3	0·003	0·0002	0·2	200		
Hf	10	0·02	0·001	0·5			
Fe	0·2	9	0·45	0·5	2	0·05	2
Mn	0·1	0·0006	0·0003	0·02	0·1	0·001	0·0003
Mo	1	0·1	0·005	0·05	30	0·1	5
Ni	0·5	9	0·45	0·1	10	0·04	0·5
P	2	0·02	0·001	20		0·01	15
K	1	0·08	0·004	0·1	0·01		100
Se	0·2	0·02	0·003				200
Si	2	1	0·05	0·1		0·1	
Ag	0·2	0·1	0·005		0·5	0·1	1
Na	7	0·007	0·0004	0·1	0·002		
S	10	4	0·01				5
Ta	2	0·007	0·0004	1			
Sn	6	0·2	0·01		10		2
W	0·2	0·003	0·0002	0·5		0·4	
U	0·06	0·01	0·0005	1	10	0·7	
Zn	1·5	0·04	0·002	2	2000	0·02	10
Zr	5	0·3	0·02	0·1		0·1	

* By the Oak Ridge National Laboratory Activation Analysis Group.
† Based on measurement of 40 disintegrations per second of radioactivity produced in an irradiation at a neutron flux (neutrons cm^{-2} sec^{-1}) indicated for a "saturation" or one-week irradiation, whichever is shorter.

Table 2 shows Leddicotte's[5] interpretation of the possibilities of the neutron activation analysis for trace element impurities in metals and alloys. The comparison study by Meinke[6] in which the limits of measurement of neutron radioactivation has been compared with that obtained by several other methods of analysis has been used in part to compile *Table 2.* These comparisons show that a radioactivation analysis method using neutrons as the nuclear particles may be inherently more sensitive than most other analytical methods. Increased neutron fluxes, *i.e.*, greater than 10^{13} neutrons cm^{-2} sec^{-1}, will greatly enhance the limits of measurement by neutron radioactivation.

Radioactivation analysis is a most specific analysis method in that the radionuclide of an element produced by a nuclear particle irradiation disintegrates in a manner unique only to that radioactive species. The characteristic half-life of the radionuclide and the type of radiations emitted in its decay are never exactly duplicated by any other radionuclide product so that it is possible to detect and identify the radioactivity of interest without too much difficulty.

Radioactivation analysis is also greatly favoured because of its almost complete freedom from the spurious contamination that is most common with other analytical methods. Unless the trace element is added to the sample in some manner *before* the nuclear particle irradiation, contamination in very high orders of magnitude can be tolerated without seriously affecting the analysis.

The limitations of radioactivation analysis have been recognized. Smales[7] classifies these as being physical, chemical and nuclear. The heat tolerance and the effective physical area available for irradiation are usually considered as physical limitations. Typical examples of irradiation facilities used in radioactivation analysis are given elsewhere in this report. With regard to heat tolerance, the activation analysis programme at the Oak Ridge Laboratory frequently uses a water-cooled irradiation facility in which it is possible to irradiate gaseous, liquid, and solid samples that can withstand temperatures of 40°–50°C.

Smales[7] has stressed the importance of structural damage and decomposition processes during irradiation, and effectively describes compensations to be considered to take care of this limitation. In addition, all the experimenters using radiochemical analysis methods for the isolation of the desired radioactivity in the work described here recognize the need for obtaining a radiochemically pure, *i.e.*, free of radioactive contaminant, separated radionuclide to complete an analysis. Each in his own way has established the " best " separations method for his particular problem and gives a description of his method for each example that is cited.

With regard to nuclear limitations, each experimenter has also considered these in the light of the type of analysis that is required to complete his problem. Most sample materials when analysed have been found to be virtually transparent to the impinging nuclear particles. However, in those instances where the sample contains a relatively large amount of some material of high cross-section, a neutron particle flux attenuation, or slowing-down of the particles as they pass through the sample, can result in a lower production of radioactivity than would be expected, since the inner portion of the sample is exposed to a lower nuclear particle flux than the outer portion. The presence of appreciable absorption, or self-shielding, can be compensated for either (1) by employing a smaller sample in analysis, or (2) by diluting the sample with a diluent of low cross-section, or (3) by using comparator or standard samples made up to contain a known amount of the element determined for in a mixture containing an amount of the nuclear particle absorbing material equal to that contained in the unknown sample, or (4) by correcting for self-shielding by means of a suitable calibration curve, separated by the use of standard. Mullins *et al.*[8] in their work on determining trace elements in zirconium–cadmium alloys by neutron radioactivation analysis have used the technique of adding to the standard sample an amount of cadmium equivalent to that in the unknown samples being irradiated. The Activation Analyses Group at O.R.N.L.[9] in its investigations on the determination of trace selenium in biological materials and trace cobalt in metals and alloys has shown that small errors can result from self-shielding even if milligram amounts of these elements are used as comparator samples. The results of this study

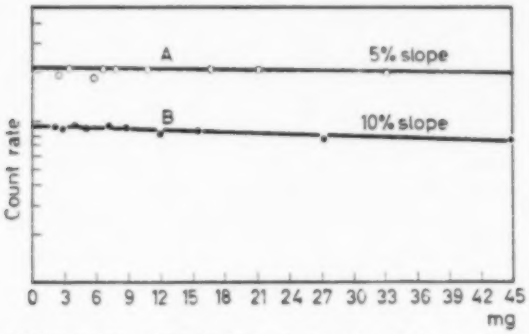

Figure 1. Self-shadowing effects during a neutron irradiation: A, $^{74}Se(n,\gamma)^{75}Se$; B, $^{59}Co(n,\gamma)^{60}Co$

are given in *Figure 1*. Similarly, Guinn and Wagner[10] recently reported the results obtained in the analysis of a series of organic samples of increasing chlorine content and show a typical calibration curve used in their study.

In those areas of nuclear limitation concerned either with the production of the same radionuclide by some other type of nuclear reaction, or by a second nuclear particle reaction upon the stable decay product of the radionuclide produced by an original nuclear reaction, it has been possible to use a pre-irradiation separation of the trace element by chemical means with a subsequent irradiation of the separated materials, or irradiations in a flux area of a nuclear particle source essentially free of the type of nuclear particle capable of producing an additional amount of the desired radionuclide, or differential counting techniques. For example, the Activation Analyses Group at O.R.N.L.[9] has used thallium sulphide as a carrier agent for manganese-55 in order to determine microgram amounts of manganese in iron. The radioactivity produced by the primary nuclear particle reaction $^{55}Mn(n,\gamma)^{56}Mn$ is greatly distorted by the amount of radioactivity produced in the reaction $^{56}Fe(n,p)^{56}Mn$. Thus, by putting the unknown sample into solution and adding a known amount of thallium as a carrier reagent, and subsequently precipitating the thallium plus manganese as a sulphide, and then irradiating the separated sulphide in a neutron flux for several hours, it was possible to determine microgram concentrations of manganese in an iron sample. Following the irradiation, the $^{56}Mn(t_{\frac{1}{2}} = 2{\cdot}56$ h) was separated by a radiochemical analysis method. Similar pre-separation techniques must be used if phosphorus is to be determined in silicon and its compounds. Long irradiation intervals are required in a radioactivation analysis for ^{31}P and appreciable amounts of $^{32}P(t_{\frac{1}{2}} = 14{\cdot}3$ d) radioactivity can be produced by the radioactivation of the stable ^{31}P formed from the decay of $^{31}Si(t_{\frac{1}{2}} = 2{\cdot}6$ h) produced in the activation of ^{30}Si by the neutron reaction $^{30}Si(n,\gamma)^{31}Si$.

An example of the production of the same radionuclide by another nuclear reaction is found in the work of Leddicotte and Reynolds[11] and Plumb and Silverman[12] on determining microgram amounts of sodium in aluminium. The primary nuclear reaction is $^{23}Na(n,\gamma)^{24}Na$; however, copious quantities of $^{24}Na(t_{\frac{1}{2}} = 15$ h) are also produced by the fast neutron reaction, $^{27}Al(n,\alpha)^{24}Na$. In these investigations, it was possible to eliminate

this fast neutron interference by irradiating in an area of the Oak Ridge Graphite Reactor completely free of high energy neutrons. Although thermal neutron flux levels of somewhat smaller magnitude were used, the limits of measurement, parts/million, were increased by the use of samples of large size (2–10 g).

As a further example of another nuclear limitation, it is known that wherever microgram amounts of arsenic are being determined in germanium and germanium tetrachloride by the thermal neutron reaction $^{75}As(n,\gamma)^{76}As$, compensation must be made for the production of ^{77}As ($t_{\frac{1}{2}} = 40$ h) by the neutron reaction $^{76}Ge(n,\gamma)^{77}Ge \xrightarrow{12\,h,\ \beta^-,\gamma} {}^{77}As$. This difficulty has been resolved by differentiating between the radiations emitted by the two arsenic isotopes by means of counting techniques involving both beta and gamma counting. Green and Kafalas[13] report on the use of neutron radioactivation analysis to determine trace arsenic in purified germanium. Samples from this study were analysed by the Activation Analyses Group at Oak Ridge National Laboratory and the results obtained showed that arsenic-75 in concentrations as small as $6{\cdot}3 \times 10^{-10}$ mole fraction of arsenic trichloride could be easily determined by this technique.

As these examples show, it is possible to overcome most of the inherent problems based upon nuclear limitations.

RADIOACTIVATION ANALYSIS METHODS

Any nuclear particle reaction producing a radionuclide can be used in radioactivation analysis. In the United States, alpha particles, protons, deuterons and fast and thermal neutrons have been used as the activity particles. It is significant that radioactivation by use of charged particles from a charged particle accelerator such as a cyclotron has had little use after 1950. At this time, reactor facilities were becoming available to most researchers and the rigid requirements on the type and size of samples that could be irradiated were relaxed. The heat dissipated within the accelerator chamber and the small area of the beam define these requirements. Another difficulty that greatly limits the charged particle method is that many different nuclear reactions can occur simultaneously during an irradiation, so that competitive reactions greatly influence the facility with which an element could be determined. Thus, the availability of the high neutron flux from various nuclear reactions, and the ease with which neutrons could be produced from targets inserted into Van de Graaff accelerators, have made it possible for most American scientists to promote neutron radioactivation analysis.

Research workers in the geographical areas in proximity to the reactor facilities of the U.S. Atomic Energy Commission have found much use for neutron radioactivation analysis in their problems. However, the most significant effort in neutron radioactivation analysis has been that accomplished at the Oak Ridge National Laboratory. Here, the advantages in the use of this method of analysis for problems arising in the research and development efforts of the Laboratory were soon realized, and in 1950 an Activation Analyses Group was formed within the Laboratory's Analytical Chemistry Division[14]. This analysis group has done considerable research

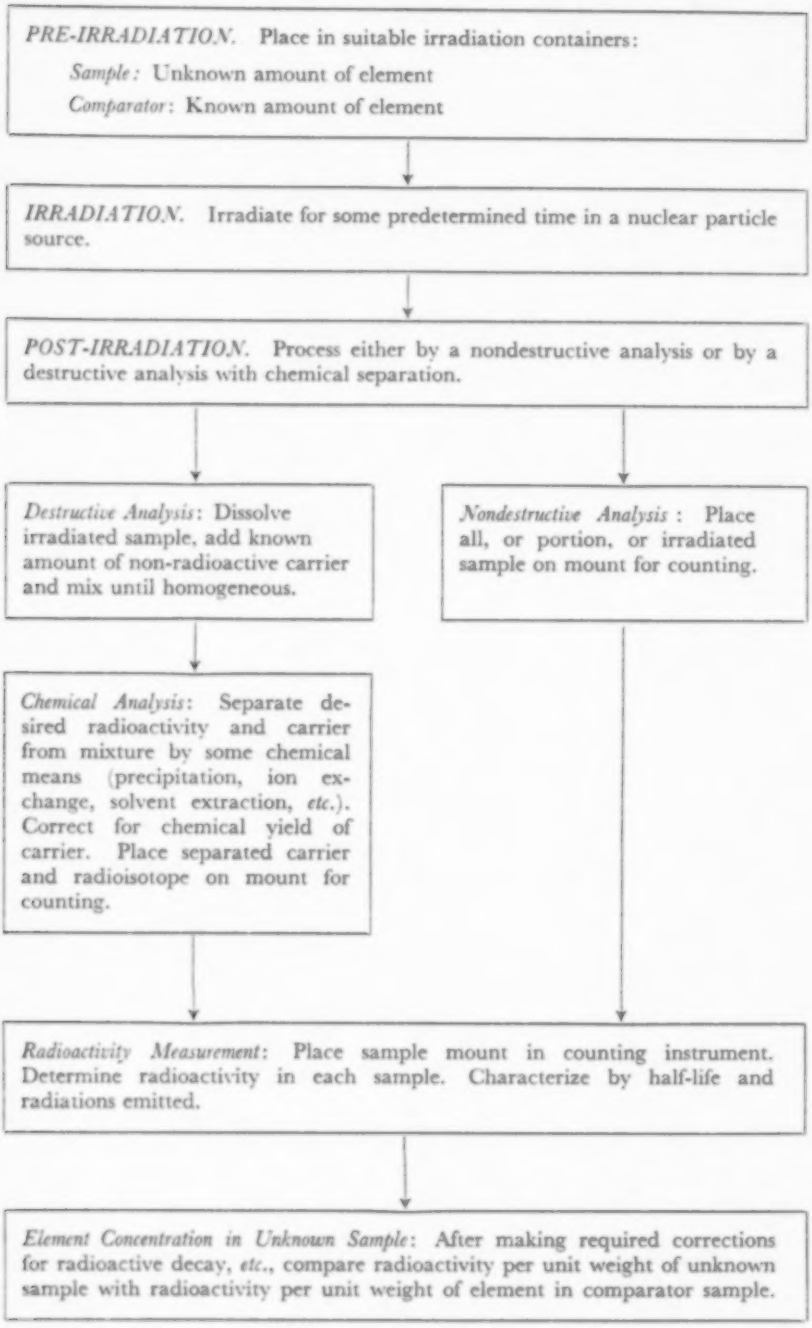
PRE-IRRADIATION. Place in suitable irradiation containers:
Sample: Unknown amount of element
Comparator: Known amount of element
IRRADIATION. Irradiate for some predetermined time in a nuclear particle source.
POST-IRRADIATION. Process either by a nondestructive analysis or by a destructive analysis with chemical separation.
Destructive Analysis: Dissolve irradiated sample, add known amount of non-radioactive carrier and mix until homogeneous.
Nondestructive Analysis : Place all, or portion, or irradiated sample on mount for counting.
Chemical Analysis: Separate desired radioactivity and carrier from mixture by some chemical means (precipitation, ion exchange, solvent extraction, *etc.*). Correct for chemical yield of carrier. Place separated carrier and radioisotope on mount for counting.
Radioactivity Measurement: Place sample mount in counting instrument. Determine radioactivity in each sample. Characterize by half-life and radiations emitted.
Element Concentration in Unknown Sample: After making required corrections for radioactive decay, *etc.*, compare radioactivity per unit weight of unknown sample with radioactivity per unit weight of element in comparator sample.

Figure 2. A typical procedure for radioactivation analysis

and development in neutron radioactivation analysis and, in addition to assisting in the Laboratory's programme, it provides a service analysis for industry, various research organizations and government agencies, particularly those with problems in trace element determinations. Thus, a considerable number of the applications in neutron activation analysis by this analysis group will be presented throughout this paper.

GENERAL PROCEDURE OF ANALYSIS

Most of the American investigators, particularly those involved in elemental microanalysis, follow an activation analysis procedure similar to that shown in *Figure 2*.

In almost all investigations, the sample materials as they are received are placed in some type of irradiation container. A typical irradiation facility used in neutron radioactivation analysis at the Oak Ridge National Laboratory is shown in *Figure 3*. Many different types of containers have been found suitable for use in radioactivation analysis and can be chosen for any particular experiment.

The period of irradiation is usually determined by the half-life of the radionuclide and the accessibility of a nuclear particle flux. However, in general, arbitrary values of at least one half-life or one week, whichever is shorter, is the basis for most analyses, especially those being completed by neutron radioactivation analysis.

The post-irradiation processing of an irradiated sample is usually dependent upon the desires of the analyst and the radioactivity measuring equipment available in his laboratory. Radiochemical procedures have been most frequently used; however, at the O.R.N.L. a considerable number of analyses are being completed by nondestructive methods[15].

From radioactivation analysis have evolved many useful radiochemical methods based upon techniques involving precipitation, ion exchange,

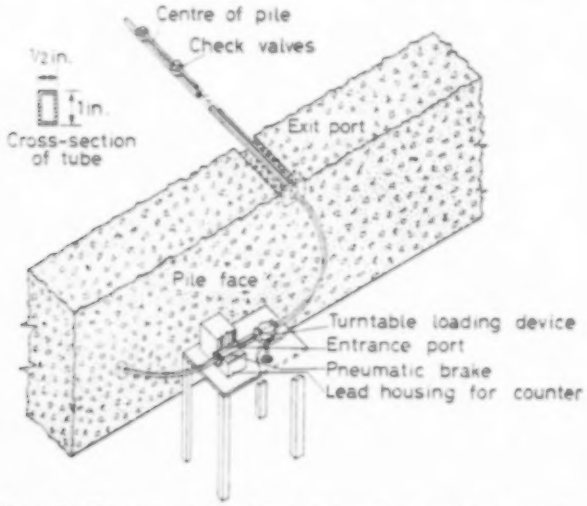

Figure 3. Fast pneumatic tube—Oak Ridge National Laboratory

solvent extraction, electrolysis, *etc.* Typical precipitation radiochemical analysis methods used in determining the constituents of aluminium-base alloys have been reported by Brooksbank *et al.*[16] Excellent examples of other quantitative analysis methods can be found in many of the references given to this report. Another report[17] has provided the outline of a qualitative analysis scheme that is used routinely in neutron radioactivation analysis at the Oak Ridge National Laboratory. The Oak Ridge group[9] has also found much use for the ion-exchange techniques given by Kraus *et al.*[18] and Gilbert *et al.*[19] in its radioactivation analysis applications.

In the measurement of the radioactivity, the beta radiations from a radioisotope after its isolation can be measured best by means of a Geiger counting technique. The recently developed technique of gamma scintillation spectrometry can be used in conjunction with radioactivation analysis to determine many of the isolated radionuclides. The principles of this method have been described elsewhere[4, 20]. Typical spectral data obtained by this method are given in several reports[10, 21–24].

The general analysis method outlined above results in the greatest sensitivity. Modifications of the method certainly can be instituted to increase this sensitivity.

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SCOPE OF APPLICATION

Solid, liquid and gaseous materials are now being analysed by radioactivation analysis methods. Submicrogram and microgram concentrations of at least seventy-five of the elements have been determined in these investigations. Applications in macroanalysis are also reported and the use of radioactivation analysis, particularly with neutrons, as a complementary method to other analysis techniques has also been reported.

This discussion concludes with a description of selected examples of the applications being made by American scientists of radioactivation analysis methods. Where appropriate, the information is given in tabular form.

Charged particle radioactivation analysis

American work on charged particle radioactivation analysis has been somewhat more limited than on the Continent. This is probably caused by the fact that more nuclear reactors have been available and much work has gone into these efforts, while charged particle accelerators have been used in basic research programmes. As early as 1938, Seaborg and Livingood[25] used cyclotron deuterons for determining gallium in iron, copper in nickel and iron in cobalt. King and Henderson[26] used alpha particles to determine small amounts of copper in silver. A summary of these applications is presented in *Table 3.*

Table 3. Charged particle radioactivation analysis

Analysis for	*Reaction*	*Material analysed*	*Element found*	*Ref.*
Ga	$^{69}Ga(d,p)^{70}Ga$ $^{71}Ga(d,p)^{72}Ga$	Iron	10^{-6} g	25
Fe	$^{58}Fe(d,p)^{59}Fe$	Co_2O_3	10^{-6} g	25
Cu	$^{63}Cu(a,n)^{66}Ga$	Ag	10^{-5} g	26

Radioactivation analysis with high intensity alpha sources

Reiffel[27] reports on the use of a 30-curie polonium source to initiate an (α,n) reaction upon beryllium-9 to determine microgram concentrations of beryllium. A prompt gamma of 4·5 MeV is given off which is measured by gamma counting. A typical apparatus used in this analysis has been described by Reiffel.

Radioactivation analysis with neutrons

Many uses for neutron activation analysis have been found by American scientists. In most instances, quantitative analyses have been completed by the use of neutrons from different neutron sources. However, the O.R.N.L. group[9] has used reactor neutrons in many qualitative applications in this radioactivation analysis method. Some of these have been completed by qualitative schemes similar to that outlined elsewhere[17] while other analyses have been completed by nondestructive or direct radioactivity measurement methods[15]. One of the examples given in this description was concerned with the determination of trace elements in beryllium metal. *Figure 4* shows the results obtained in an analysis by means of a gamma scintillation spectrometer equipped with a multichannel analyser and by radioactive decay measurements. More recently, Leddicotte and Bate[28] have used similar methods of analysis by means of a 200-channel analyser to determine qualitatively trace elements in tobacco, limestone, zinc ore, cement, graphite and sand.

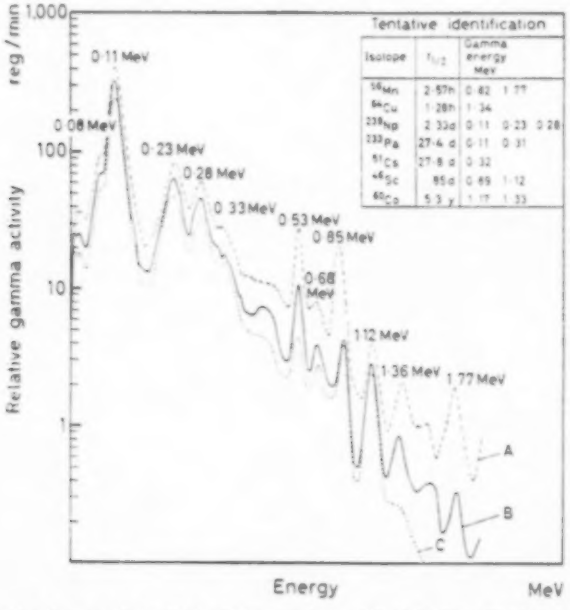

Figure 4. Activation analysis of beryllium metal. Irradiation period: 155 h. Flux: $6{\cdot}5 \times 10^{11}$ neutrons cm^{-2} sec^{-1}. Instrument: 20-channel gamma scintillation spectrometer. Crystal: solid NaI. Spectra recorded: A, 11 h; B, 30 h; C, 52 h after reactor discharge

Table 4. Fast neutron radioactivation analysis

Neutron energy (MeV)	*Nuclear source*	*Flux* (neutrons cm^{-2} sec^{-1})	*Analysis for*	*Neutron reaction*	*Material analysed*	*Element content* (g)	*Ref.*
14·0	Low voltage accelerators (100–250 kV), D–T reaction	5×10^7	Si	$^{28}Si(n,p)^{28}Al$	SiO_2	0·4	29
14·0	Low voltage accelerators (100–250 kV), D–T reaction	5×10^7	Al	$^{27}Al(n,\alpha)^{24}Na$	Al_2O_3	0·4	29
2·3	Reactor	10^9–10^{10}	S	$^{32}S(n,p)^{32}P$	HF, fluoride salts	10^{-6}	52
4·5	Reactor	$>10^9$	Ni	$^{58}Ni(n,p)^{58}Co$	Soils, metals, ores	10^{-6}	52
	Reactor	$>10^9$	Ti	$^{46}Ti(n,p)^{46}Sc$	Metals	10^{-5}–10^{-6}	52
8·3	Reactor	10^8–10^{10}	Al	$^{27}Al(n,\alpha)^{24}Na$	Water	$<10^{-6}$	30

Although most of these applications have been made with slow or thermal neutrons, examples of fast neutron radioactivation are beginning to be reported. Turner[29] has determined silicon and aluminium with fast neutrons produced by an accelerator. Leddicotte *et al.*[30] have recently used fast neutrons from a reactor to determine trace sulphur, nickel, titanium and aluminium (see *Table 4*). In addition to fast neutron reactions, Bate and Leddicotte[31] have been using *tritons* produced in the interaction of neutrons with ^6Li in the nuclear reaction $^6Li(n,\alpha)^3H$, to determine microgram concentrations of oxygen in lithium, zirconium, aluminium and tantalum metals by the secondary nuclear reaction $^{16}O(n,t)^{18}F$. Fluorine-18 decays with positron emission and a half-life of 112 min.

APPLICATIONS OF NEUTRON RADIOACTIVATION ANALYSIS

Use of accelerators as neutron sources

Low voltage accelerators of the Cockroft–Walton and Van de Graaff types have been used in a number of radioactivation analysis applications. In particular, the fast neutrons produced at voltages of 100–200 kV and with a deuterium–tritium target have been used for determining silicon and aluminium[29]. The results of this work are given in *Table 4*.

Prolific neutron outputs are obtainable from Van de Graaff positive-ion accelerators by means of the $^9Be(d,n)^{10}B$ reaction. Burrell and Gale[32] have tabulated the limits of measurements for irradiations at a flux of 10^9 neutrons cm^{-2} sec^{-1}. Typical information obtained in the use of this method of radioactivation analysis by several other research workers[10, 33] is given in *Table 5*.

Use of low intensity neutron sources

Meinke and Anderson[34] have used a 25 mg radium–beryllium neutron source to develop a method for the activation analysis of rhodium, silver and indium in concentrations of 1 per cent or more. In another study, Meinke and Anderson[35] have reported on the determination of europium

Table 5. The use of Van de Graaff accelerators in radioactivation analysis

Material analysed	*Element determined*	*Obs. conc.* (parts/million)	*Ref.*
Brominated polymers	Br	20–40	33
Synthetics	Cl	10^2–10^3	33
NH_4I, CaI_2	I	50–66	33
NH_4F, NaF, LiF, Organics	F	10^2–10^3	33
Polymers	Cl	3–190	10
Re-forming catalysts	Pt, Cl	10^3	10
Inhibited sulphuric acid	Na, As	10^3	10

in the presence of samarium and of dysprosium in the presence of holmium by use of similar equipment and techniques. De and Meinke[24] have recently used a 1–5 curie antimony–beryllium source and nondestructive methods based upon gamma scintillation spectrometry to analyse silver–cobaltic oxide, silver–lead iodide, copper and aluminium in synthetics, sodium iodide in various mixtures with other salts, manganese in ferromanganese and in various other mixtures. More recently Strain *et al.*[36] have been using americium–boron, americium–beryllium and radium–beryllium sources and an irradiation time of 1 h or less to determine a number of elements in concentrations of 0·1 per cent or less. Typical results from this unpublished study are given in *Table 6*.

Table 6. Neutron radioactivation analysis with low intensity neutron sources*

Element	*Irradiation time*	*Units per minute† from the detection of 1 mg of element*
Sc	1 min	54·3
Co	10 min	2·8
Mn	1 h	17·2
Cu	1 h	1·0
^{238}U	0·5 h	20·0
Na	1 h	0·2
Al	5 min	1·0

* J. E. Strain *et al.*, O.R.N.L. Activation Analyses Group.
† Detection limits for gamma scintillation count at discrete gamma energies. Count rate expressed as total scaler unit counts in channel of maximum energy. 1 unit = 16 counts per minute.

All of these studies would indicate that apparatus employing low intensity neutron sources can be applied to many analysis problems concerned with determining many different elements in which these occur in macro concentrations. Less time for analysis, smaller sample sizes and, in many instances, non-destructive analysis of sample material can result from the use of such apparatus.

Use of reactor neutrons

The application of large reactor neutron sources is well defined. Boyd[1], Taylor and Havens[2] and Leddicotte and Reynolds[3, 37], in particular, have based much of their descriptions of radioactivation analysis upon the use of the prolific sources of neutrons from a nuclear reactor. Leddicotte and Reynolds[37] and Leddicotte[38] have described the types of sample materials to which neutron radioactivation analysis can be applied.

Applications in biochemistry

Table 7 shows the use of neutron radioactivation analysis in biochemistry by a number of investigators. Its use in medical research is most prominent; however, some work has already begun on its applications to the problems of nutrients, plant ecology, *etc.*

Table 7. Neutron radioactivation analysis applications in biochemistry

Element determined	*Material analysed*	*Element found* (g)	*Ref.*
	In medical research		
Na	Blood serum	10^{-2}	39
	Muscle		40, 41
	Bone		42
	Blood vessels		43
	Tissue		44
K	Muscle	10^{-2}	40, 41
	Tissue		44
P	Muscle	10^{-4}	40, 41
Cl	Blood vessels	10^{-4}	43
Co	Tissue	10^{-7}–10^{-6}	44
Sb	Tissue	10^{-6}–10^{-5}	44
As	Tissue	10^{-9}–10^{-6}	44
Br	Tissue	10^{-6}–10^{-5}	44
Cd	Tissue	10^{-6}	44
Cs	Tissue	10^{-6}–10^{-5}	44
Cu	Tissue	10^{-7}–10^{-4}	44
Ni	Tissue	10^{-7}–10^{-6}	44
Rb	Tissue	10^{-5}–10^{-4}	44
Se	Tissue	10^{-9}–10^{-5}	44
Sr	Tissue	10^{-6}–10^{-5}	44, 45
	Bone		46
Zn	Tissue	10^{-6}–10^{-3}	44, 47
Zr	Tissue	10^{-6}–10^{-5}	44
Mn	Tissue	10^{-6}	22
I	Blood proteins	10^{-10}–10^{-6}	44, 48
Au	Tissue	10^{-8}–10^{-6}	49, 50
	Other biochemistry applications		
Co	Plant ash	10^{-9}	51
	Sugar cane	10^{-7}–10^{-6}	52
	Faeces	10^{-8}–10^{-6}	45
V	Plant ash	10^{-9}	51
Se	Soybean meal, yeasts, kidney powders	10^{-8}–10^{-5}	53, 54
	L-cystine		55
Cu	Sugar cane	10^{-6}	52
Fe	Grasses and grains	10^{-4}–10^{-3}	52
Mo	Sugar cane	10^{-7}–10^{-6}	52

Applications in petrochemistry

An extensive study of at least twenty trace elements in petroleum and similar materials has been recently completed by the Activation Analyses Group at O.R.N.L.[9] A report of this work is now being compiled. Typical information obtained in the neutron radioactivation analysis of nickel in silica–alumina catalysts is given in *Table 8*. The data obtained are compared with those from the analysis of the same material by other methods. Work by other researchers[10, 45, 56] also shows the usefulness of neutron radioactivation analysis in trace element determinations in

Table 8. Determination of nickel in silica–alumina catalysts

Sample	*Nickel per cent by weight*					
	Neutron activation analysis	*Chemical colorimetric*	*Electrolysis colorimetric*	*Chemical gravimetric*	*Spec.*	*X-ray*
A Base material	0·00095	0·00045	0·00065			
Base + 0·005%	0·0052	0·005	0·0056			
Base + 0·01%	0·0114	0·010	0·0104			
Base + 0·018%	0·0224	0·0197	0·0190			
D	0·0075			0·0090	0·0110	0·008
E	0·0145			0·0140	0·0170	0·0170
F	0·0120			0·0110	0·0090	0·0130

petrochemicals. In particular Guinn's report[10] shows the possibilities of the method in analysing on a routine basis, and with nondestructive techniques, some twenty-seven different elements in petrochemicals. Many of these can be analysed in concentrations as small as a few parts per million.

Applications in metallurgy

Most of the applications of neutron activation analysis have been made in determining trace elements in metals and alloys. One of these[57] has been used in studies concerned with the reduction of the iron and nickel contents of zirconium iodide by a floating zone purification of zirconium. The data obtained by the Activation Analyses Group at O.R.N.L.[9] were used in the preparation of the curve given in *Figure 5* to show the distribution of nickel as a function of displacement after several passes of the molten zone. More recently this analysis group has been concerned with the determination of trace impurities in ultra-pure semiconductor materials and in silicon and its compounds[5]. Typical data obtained in some of this work are given in *Table 9*. In addition to this work, Leddicotte *et al.*[52]

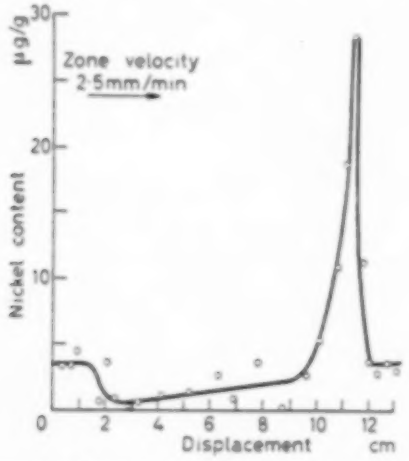

Figure 5. Nickel content as a function of displacement after six passes of the molten zone

Table 9. Radioactivation analysis of trace elements in semi-conductor materials

Material	*Analyses for*	*Element found* (parts/million)
Trichlorosilane	Cu	$0{\cdot}4 \times 10^{-3}$
	Na	$25{\cdot}0 \times 10^{-3}$
	Mg, Ti, Al, Fe, Sn	$<15 \times 10^{-3}$
	Ag, Sb, Mn, As	$<10^{-3}$
Arsenic	Se	0·37, 0·36, 0·38
	Te	12·12
	S	69·6, 64·1
		5·0, 6·7
Gallium	Na	268, 260
	Zn	25, 26
	Sn	1·0
	Cu	2·0
	Pt	3·2
	In	0·17
	W	0·018
	Hg	0·68

Table 10. Some applications of radioactivation analysis in metallurgy

Element determined	*Material*	*Element content* (g)	*Ref.*
Au	Silicon	10^{-7}–10^{-6}	58
Zn	Silicon	10^{-4}	59
	Aluminium	10^{-3}	16
	Tungsten	10^{-5}	60
As	Silicon	10^{-6}	59
	Tungsten	10^{-6}	60
	Germanium	10^{-4}	61
W	Silicon	10^{-7}	59
	Titanium	10^{-6}	23
Fe	Silicon	10^{-5}	59
	Tungsten	10^{-4}	60
K	Silicon	10^{-7}	59
	Tungsten	10^{-6}	60
Na	Silicon	10^{-8}	59
	Tungsten	10^{-6}	60
	Germanium	10^{-5}	61
Ta	Silicon	10^{-6}	59
Cu	Aluminium	10^{-5}	59
	Aluminium	10^{-6}–10^{-4}	16
	Tungsten	10^{-6}	60
	Germanium	10^{-4}–10^{-6}	61, 62
Cr	Aluminium	10^{-6}	59
	Tungsten	10^{-4}	60
O	Metals	10^{-4}–10^{-6}	31
Mn	Beryllium	10^{-5}–10^{-4}	45
Ti	Aluminium	10^{-3}	16
Mo	Tungsten	10^{-6}	60
Sn	Tungsten	10^{-4}	60
Ga	Germanium	10^{-6}	61
	Aluminium	10^{-6}	45
Zr	Zr–Hf	10^{-2}	63

have reported many other applications at the Oak Ridge National Laboratory.

Applications of neutron activation analysis in the field of metallurgy by other American investigators are shown in *Table 10*.

Applications in geochemistry

Important studies have been undertaken to determine trace elements in meteorites, ores, soils, waters, *etc.* by neutron activation analysis. Typical applications are given in *Table 11*.

Table 11. Applications of neutron radioactivation analysis in geochemistry

Element determined	*Type of sample*	*Element content (g)*	*Ref.*
Au	Meteorites	10^{-7}–10^{-6}	64
Re	Meteorites	10^{-6}	65
K (as ^{41}A)	Minerals	(Age dating)	66
Th	Thorium meteorites	10^{-11}	67
	Stone meteorites	10^{-6}	68
	Ores, water, soils	10^{-8}–10^{-6}	69
	Minerals	10^{-9}	70
U	Stone meteorites	10^{-8}	71
	Phosphate ores		72
Bi	Stone meteorites	10^{-10}	73
Pb	Stone meteorites	10^{-7}	73
Tl	Stone meteorites	10^{-10}	73
Mn	Water	10^{-6}	74
Various	Water	10^{-10}–10^{-5}	75

Miscellaneous applications

Miscellaneous applications of neutron radioactivations include the analysis of 10^{-9} g of antimony in zirconium oxide[76]. Cosgrove *et al.*[77] have used neutron radioactivation for the determination of 10^{-6} g of chloride, 10^{-6} g of iodide and 10^{-9} g of bromide in studies of the luminescent qualities of zinc sulphide phosphorus. Brooksbank *et al.*[45] also report on determining 10^{-5}–10^{-6} g of cadmium in vinylite resins. Sayre *et al.*[21] have used neutron activation analysis and gamma scintillation spectrometry to determine the presence of Al, Mn, Na, La, Sm, Cr, Sc, Cs, Fe, Co and Eu in ancient pottery. Rona *et al.*[74] have determined 10^{-6} g of manganese in oceanographic studies.

In addition to these analyses, Leddicotte[78] has determined the isotopic ratio of ^{235}U to ^{238}U in shales, and Rona[70] has used neutron radioactivation analysis for ^{232}Th/^{230}Th isotopic ratios. Emery and Leddicotte[79] have used neutron radioactivation analysis in the determination of trace argon in gaseous mixtures.

Radioactivation analysis as a complementary technique

A number of analytical methods have been complemented by radioactivation analysis. Benson[51] reports on its use as a complement to radioautography of tissue specimens. Leddicotte *et al.*[80] have used it to assist in the analysis of particle size distribution in thorium oxide and uranium

oxide samples, and it has been used in studies of particle size distributions in multicomponent systems.[81] In addition, Leddicotte and Bate[82] have used it in studying the diffusion rates of chromium in Inconel in contact with corrosive solutions. Schultz *et al.*[83] have used radioactivation analysis to measure gear wear in various types of lubricants. Each of these applications is aptly described in these reports and data are presented for each application.

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DISCUSSION

G. B. Cook (*U.K.*): What safety factors do you impose on samples so that they should not endanger the reactor? I am thinking, for instance, of organic liquids and solids which may also be inflammable and which, under the action of the intense ionizing radiation, may decompose and build up dangerous pressures in sealed containers.

G. W. Leddicotte (*U.S.A.*): The containers used satisfy the requirements of the Reactor Safeguards Committee. They are never filled to more than about one-third of their volume so that sufficient room is left to allow for pressure effects. By July 1960, there will be a vertical facility with a cross-section of about 4 in. surrounded by a shield to permit the pouring in of liquid nitrogen or water.

J. Hoste (*Belgium*): When chemical separations are required after activation it is of advantage to use specific reagents to speed up the process and reduce contamination. Copper, for instance, can be extracted specifically with isoamyl alcohol as the diquinolyl complex. As regards the difficulties mentioned in connection with the isolation and purification of chromium, the chromium can be isolated by distillation as CrO_2Cl_2 from perchloric acid through which hydrogen chloride is passed. The yield is quantitative. Other volatile chlorides such as those of arsenic, antimony and tin can be removed before the CrO_2Cl_2 distillation.

W. W. Meinke (*U.S.A.*): I should be interested to hear further details about the pricing of radioactivation analysis.

P. Leveque (*France*): The fee in France is 50 new French francs per analysis, including the irradiation. The price is not a cost price; as the method is relatively new, the price has been fixed as low as possible.

G. W. Leddicotte (*U.S.A.*): The price in the United States was originally fixed on an analysis-hour basis. The original price was $35 per element, taking into account the analytical time and the cost of buying neutrons at the reactor. More recently, a price of $16 has been fixed for any irradiation service; monitoring would cost a further $35, bringing the total to $51 per irradiation. The object is to cover costs and, once a procedure becomes routine and can be taken over by commercial firms, the general policy is to discontinue the service.

D. Gibbons (*U.K.*): There is no fixed scale of charges for the Harwell industrial activation analysis service. The charge for each analysis is made up of the cost of the radiation plus the cost of the experimental work in terms of the number of man-hours involved in the actual analysis. No charge is made for development work, which is regarded as research. We are not prepared, however, to undertake routine repetitive analyses for a large number of samples. Under such circumstances it would be in the interest of the user to set up his own laboratory. The average cost for the last 250 samples was £5 each. This may seem rather low, but the majority of irradiations have included up to about six samples so that the contribution of the irradiation charge per sample is small. Our irradiation charges have been increased and I estimate that the average charge will in future be £6 to £8 per sample and this will, of course, be higher for a single analysis and lower for multiple analyses.

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RADIOACTIVATION ANALYSIS IN BIOCHEMISTRY AND MEDICINE

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L'analyse chimique est un auxiliaire essentiel de la recherche biochimique. Depuis quelques années, de nouvelles techniques d'analyse telles que l'emploi des traceurs radioactifs, l'échange d'ions et la chromatographie donnent de bons résultats. L'analyse par radioactivation déjà appliquée avec succès—quoique de manière assez restreinte—en biochimie humaine et animale, est probablement appelée à jouer un rôle de plus en plus utile dans l'une et l'autre sciences. Les avantages de la méthode: simplicité, rapidité, sensibilité et précision, ont été mis à profit de façon limitée en odontologie, en médecine légale et dans la recherche sur le cancer. Dans ces domaines de la recherche clinique, comme dans d'autres, un grand nombre de problèmes intéressants paraissent pouvoir être étudiés par cette méthode.

Jusqu'à maintenant, en biochimie, l'analyse par activation est surtout appliquée aux échantillons de tissus, en vue de la recherche non seulement d'éléments à l'état de traces, mais aussi de constituants plus courants (tels que le sodium et le potassium), lorsque les autres méthodes manquent de sensibilité ou sont incommodes. Le métabolisme de certains éléments, comme le strontium, ne peut être que partiellement déterminé au moyen des traceurs radioactifs ou des procédés classiques de la biochimie. Les méthodes par activation permettent d'étudier la répartition de l'élément normal dans les tissus et les excreta.

La combinaison de l'activation neutronique et de la chromatographie sur papier a l'avantage d'augmenter la sélectivité et la sensibilité. La plupart des applications de l'analyse par radioactivation en biochimie supposent l'utilisation d'un réacteur nucléaire, mais des mesures ordinaires, rapides et exactes, du taux de sodium sanguin peuvent être faites à l'aide d'une source portative de neutrons, facilement utilisable dans les hôpitaux.

L'auteur examine en détail les problèmes suivants, qui semblent pouvoir faire l'objet d'autres recherches par les techniques de radioactivation:

(1) mesure de ^{127}I lié aux protéines dans le sang humain;

(2) métabolisme du nickel chez l'homme;

(3) métabolisme des éléments à l'état de traces dans les tumeurs;

(4) rôle du manganèse dans la formation des os;

(5) rôle du vanadium dans la calcification des dents et la prévention des caries;

(6) mise en évidence de nouveaux éléments à l'état de traces, dans la nutrition humaine;

(7) étude des intoxications chroniques causées par des métaux industriels.

" All science is measurement ", said Helmholtz. This dictum might not be wholly acceptable in clinical science, but it is beyond dispute that new chemical and physical techniques for the measurement of bodily functions have contributed much to the spectacular advance of medicine during the last half-century. Radioactivation analysis is a refined, yet simple, method of investigation which has already proved serviceable to a limited extent in medicine and biochemistry. As its possibilities in these fields become more widely known, its applications will rapidly increase, particularly in the many hospitals and research laboratories already equipped for work with radioactive materials.

The place of radioactivation technique in biochemistry was reviewed extensively[1] in 1957. The present survey necessarily covers some of the same ground, but work done during the last couple of years will be noted particularly, and reference will be made to a number of problems on which future research seems likely to be rewarding.

TISSUE ANALYSIS

Some elements present in human and animal tissues are very difficult to analyse, even with the most sensitive spectrographic or colorimetric techniques. *Table 1* shows figures quoted by Koch *et al.*[2] to illustrate the range of values reported by different authorities after analysis of normal human tissue.

Table 1. Analysis of normal human tissue

Element	*Tissue*	*Concentration*	*Ref.*	*Method*
Cr	Lung ash	2500 μg/g	3	Colorimetry
		45 μg/g	2	Colorimetry
Co	Blood	0·17–1·48 μg/100 ml	4	Spectrography
		0·35–6·30 μg/100 ml	2	Radioactivation
Co	Spleen	0·47 μg/g	5	Colorimetry
		0·03 μg/g	2	Radioactivation
Cu	Liver	5 μg/g	6	Colorimetry
		11 μg/g	2	Spectrography
		25 μg/g	7	Colorimetry

For other elements, as will be noted later, similar uncertainties exist.

It is fortunate that the four substances, hydrogen, carbon, nitrogen and oxygen which constitute 96 per cent of living matter do not have any useful radioactive isotopes made by neutron bombardment of the stable elements. But for this dispensation (which is so often regretted in radioactive tracer work) the analysis of tissue by neutron activation would be virtually impossible. As it is, the task is sometimes hard enough because of the wide range of induced activities among the elements to be identified and estimated in normal or pathological tissue samples.

The contribution of an individual element to the total induced activity may be isolated in two main ways:

(1) analysis of the emitted radiation by coincidence counting, by spectroscopy or by counting through suitably chosen filters (really a simple form of spectroscopy); and
(2) chemical separation followed by radioactive assay.

These techniques are particularly important in the medical and biochemical applications of radioactivation analysis, where the samples under investigation may contain a dozen or more radioactive nuclides in appreciable amounts after irradiation.

Radioactivation analysis of the blood

The analysis of blood is a problem which illustrates the difficulties very clearly. Spencer *et al.*[8, 9] have experiments in progress using a 5-watt pool-type nuclear reactor giving a thermal neutron flux of $2{\cdot}5 \times 10^8$ neutrons $cm^{-2}\,sec^{-1}$. They calculate that irradiation of 10 ml of serum for one hour in this modest neutron flux should produce measurable activities in twelve elements (Br, Ca, Cl, Co, Cu, I, K, Mg, Mn, Na, P and Zn) (*cf. Table 2*). The estimation of sodium by this method is very easy. If the irradiated sample is left to decay for 12 h, 99·6 per cent of the residual γ-ray activity will be due to ^{24}Na. The concentration of sodium in the original specimen may then be found by a simple counting arrangement. Most of the other nuclides noted in *Table 2* decay more quickly than does the ^{24}Na and must therefore be separated promptly if their activities are to be measured.

Table 2. Activities induced in 10 ml of human blood serum after exposure for 1 h to a thermal neutron flux of $2{\cdot}5 \times 10^8$ neutrons $cm^{-2}\,sec^{-1}$

Isotope	$t_{\frac{1}{2}}$(h)	*Disintegrations/min**
^{80m}Br	4·6	2350
^{80}Br	0·3	43,500
^{82}Br	35·9	290
^{49}Ca	0·14	444
^{38}Cl	0·62	800,000
^{60m}Co	0·18	30
^{64}Cu	12·8	222
^{66}Cu	0·085	950
^{128}I	0·42	1440
^{42}K	12·5	1909
^{27}Mg	0·16	123
^{56}Mn	2·58	30
^{24}Na	15·0	320,000
^{32}P	348	35
^{69}Zn	0·87	134

* Immediately after neutron activation as specified above.

Chemical treatment of irradiated samples

Complete recovery of the desired element may not be possible, but the accuracy of the determination need not suffer. A few milligrams of the element concerned is added in suitable form as a stable carrier to the irradiated specimen. The proportion of the carrier which survives the chemical separation is readily found by conventional methods and an appropriate correction made to the counting rate observed in the assay of the radioactive sample.

Rapid chemical separation of copper and zinc from irradiated blood was achieved by Bowen[10]. ^{64}Cu($t_{\frac{1}{2}} = 12{\cdot}8$ h) was isolated with a yield of about 70 per cent and without radioactive impurities; the chemical procedures for eight samples occupied only two hours. Similar results were obtained for ^{69}Zn.

Estimation of gold in tissue

Tobias *et al.*[11] separated ^{198}Au from irradiated blood by precipitation with a stable carrier and subsequent electroplating onto a platinum

planchet. Gold is not usually considered as a constituent of human tissue and the total amount in the body is of the order of 50 μg. Tobias *et al.* were able to estimate the gold content of red cells, white cells and plasma in a 10 ml sample of blood.

Muller[12] used an ingenious technique to estimate radiation dosage in treatment with ^{198}Au. This material, in colloidal form, is used for the relief of disseminated cancer, as for example in the pleural or peritoneal cavity. Muller allowed the ^{198}Au to decay ($t_{\frac{1}{2}} = 2{\cdot}7$ d) after injection, until negligible activity remained. Small samples (1 g or less) of tissue were then removed, ashed and subjected to neutron activation. The ^{198}Au produced by this second irradiation was estimated by analysis of the complex decay curves obtained by scintillation counting over a period of two or three weeks.

Estimation of sodium, potassium and phosphorus

Tissues other than blood have also been examined by radioactivation. Reiffel *et al.*[13] were able to estimate sodium, potassium and phosphorus in muscle, using samples of a few milligrams. The induced activities in sodium and potassium were identified by counting with an end-window Geiger tube and absorbers of appropriate thickness. Phosphorus was estimated after several days' decay had reduced the other two activities to insignificant levels. An accuracy of about 5 per cent was obtained by these simple arrangements.

Druyan *et al.*[14] have recently used neutron activation analysis in the estimation of bone sodium. This estimation is usually a difficult problem, because the ratio of calcium to sodium in bone (40 to 1) makes flame photometry almost impossible. Under neutron bombardment the only calcium isotope formed in appreciable amount is ^{49}Ca, with $t_{\frac{1}{2}} = 8$ min. If counting is delayed for two hours after irradiation, this isotope, originally quite abundant, does not interfere to a noticeable extent. Gamma-ray spectrometry and half-life measurements provide further means of ensuring that only the ^{24}Na activity is counted. No chemical treatment of the irradiated bone is necessary.

TRACE ELEMENT ANALYSIS

The estimation of trace elements is a problem in which progress is often halted for lack of sufficiently sensitive analytical techniques. Radioactivation analysis offers interesting prospects here. Firstly, there may be new trace elements awaiting recognition. It is not known, for example, whether aluminium, chromium, cobalt and nickel are of any importance in human nutrition. The concentrations present in the body are near—or beyond—the limits of reliable measurement by chemical, colorimetric or spectrographic methods. Consequently there is much uncertainty about the excretion and absorption of these elements, and even about their presence in normal tissue. All four elements can be detected with good sensitivity by neutron activation. Cobalt has already been the subject of such a study[2] but more remains to be done for, as Underwood[15] points out: " no serious attempts to demonstrate an essential function for nickel, with the aid of modern experimental techniques, have yet been undertaken " and

" the occurrence of aluminium in animal tissues, blood and urine has been the subject of considerable controversy, arising largely from difficulties and errors in the analytical, especially the spectrographic, techniques employed ".

Cancer research

Tobias *et al.*[16], using radioactivation techniques, have demonstrated an increased uptake of cobalt by tumour cell nuclei in mice. Further experiments on the metabolism of trace elements in human cancer might be rewarding, particularly in view of the importance of certain of these elements in hormone or enzyme systems. The concentrations to be measured are so low and the amounts of material available so small (as, for example, in biopsy specimens) that radioactivation is the only method of analysis likely to succeed.

Rare earths in tissue

Little, if anything, is known about the biochemistry of the rare earths. Many of these elements are very suitable for radioactivation analysis, because of their large neutron capture cross-sections. Chemical separation is difficult but ion exchange has been used successfully by Brooksbank *et al.*[17] These authors found three rare earths—Er, Tm and Yb—to be present in animal bone at levels higher than 1 part/million.

Some of the rare earths, along with other uncommon elements, occur among the fission products which will be manufactured to an increasing extent through the development of atomic energy, and may sometimes be important as environmental hazards. The metabolism of these elements in plants, animals and marine organisms should obviously be studied, with particular attention to the possibility of concentration processes in food chains. In some instances, radioactivation of the naturally occurring elements, or of added stable tracers, provides a good method of making such experiments before the radioactive fission products are present in measurable quantities.

RADIOACTIVATION ANALYSIS FOR ARSENIC

Recent investigations with arsenic have demonstrated the advantages of radioactivation analysis and have suggested topics for further research or enquiry.

Arsenic and lung cancer

As Holland *et al.*[18] point out: " arsenic is the only component in cigarette smoke that is known to be carcinogenic in man ". The arsenic enters the leaf of the tobacco plant from sprays or dusts used as insecticides. Bailey *et al.*[19] analysed cigarettes from many countries, and found concentrations (expressed as As_2O_3) between 0·0 (Turkey) and 81·0 parts/million (Denmark). In one British brand the level fell from 25–100 parts/million in 1948 to 1–2 parts/million in 1956. The British manufacturers report[20] that the average arsenic content of their cigarettes in 1956 was 7 parts/million and that the decline is continuing. In the U.S.A.[18] the arsenic content of five leading brands in 1957 ranged between 42·5 and 52·0 parts/million;

the corresponding limits in 1933 were 7·5 and 30 parts/million. The proportion of the arsenic in a cigarette which is inhaled has been variously estimated at 5 per cent[20] and 11 per cent[18].

Since the daily intake of arsenic may be substantially greater in smokers than in non-smokers, it is reasonable to expect a measurable difference in excretion rates. Small samples of hair from 1000 people were recently subjected to radioactivation analysis[21] in an attempt to demonstrate such an effect. Arsenic levels were found to be the same in smokers as in non-smokers, though considerably higher in men than in women (*Figure 1*): the explanation for this unexpected finding is not known. It would be valuable to know whether the rate of arsenic excretion in the urine shows any correlation with cigarette consumption. Arsenic has been estimated in urine with excellent sensitivity by radioactivation analysis[22]. Large-scale investigations could be made reasonably quickly with small samples. In the measurements just mentioned, the range of arsenic levels found was very wide—from 0·01 to 0·33 parts/million. It is tempting to speculate whether this spread of values includes a variation related to smoking habits.

Arsenical poisoning in industry

Arsenic, for centuries a favourite instrument of homicide, is now dangerous mainly as an industrial poison. Doig[23] describes three cases of arsenical poisoning in tank cleaners, employed in removing scale from lead vessels used to store sulphuric acid. Arsenic (from pyrites) is a common contaminant of commercial sulphuric acid. The scale in the storage tanks may contain as much as 45 per cent of As_2O_3, some of which is converted into arsine—one of the most toxic gases known. In one of Doig's cases, the diagnosis of arsine poisoning was not made until several months after the victim's death, because no one in the factory associated his illness (haemolytic anaemia) with his occupation. In another case, samples of hair and nail were found by radioactivation analysis to be rich in arsenic.

Arsenical poisoning is an occupational risk in the manufacture of insecticides, weed-killers and sheep-dip. Protective clothing is not always used and other simple hygienic measures are often ignored. Some interesting measurements were made[21] on a worker from a sheep-dip factory who was admitted to hospital with a squamous carcinoma of the scrotum, attributed to chronic irritation by arsenical dust. Samples of beard hair were taken with an electric razor at intervals after the patient's admission and subjected to radioactivation analysis to measure their arsenic content. The following results were obtained:

Weeks after admission	*Arsenic content* (parts/million)
0	3·12
1	1·79
3	0·84
4	0·94

The hazards associated with the industrial uses of arsenic are not always recognized by workers and managers. In certain factories, regular inspection of hair and nail samples by radioactivation analysis would be

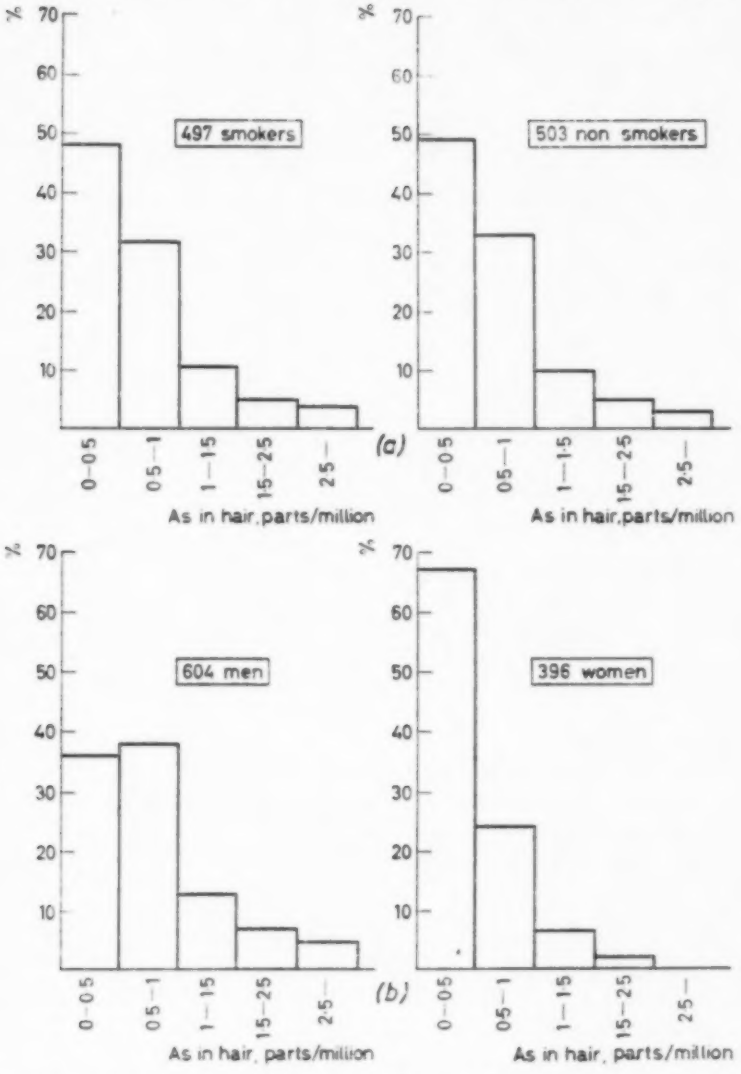

Figure 1. Arsenic levels in hair: comparison between (*a*) smokers and non-smokers, (*b*) men and women

a useful practice, providing early warning of undue contamination which might have serious consequences if not arrested. Tests of this kind are, of course, impracticable by conventional methods of analysis.

RADIOACTIVATION ANALYSIS IN DENTAL SCIENCE

Many problems in dental science await attack by activation techniques. Trace elements have an important role in the formation, preservation and

decay of teeth. Some are absorbed from cleaning or restorative materials; others occur naturally. Experimental work in human subjects is very difficult because many of the elements concerned are present at such low concentrations that a single tooth does not provide an adequate sample for analysis by chemical, colorimetric or spectrographic methods. Consequently it is often necessary to use pooled material from many different subjects, with inevitable loss of precision. The analysis of teeth is important because of the belief that susceptibility to dental caries is affected by nutritional factors during the period of enamel mineralization. At present this hypothesis can be tested only by large-scale experiments such as fluoridation of water supplies and subsequent dental examination of large numbers of children. Useful investigations could be made in a less controversial way with the help of radioactivation analysis.

Vanadium in teeth

It is known, for example, that vanadium is isomorphous with phosphorus and can replace it in the apatite lattice from which teeth are largely built. Rygh[24] found the presence of vanadium in the diet of rats and guinea pigs to have a significant effect on the mineralization of teeth during the first weeks of life. Animals restricted to vanadium-free diets showed the greatest incidence of caries. Geyer[25] found that incipient caries, produced by adjustment of the diet in Syrian hamsters, could be halted by the addition of vanadium to the food. As yet there is no convincing evidence for the presence of vanadium in normal human teeth. Detection of this element by radioactivation analysis should be possible with excellent sensitivity.

Arsenic in teeth

Arsenic is a known impurity in dental cements containing zinc. It has been suggested[26] that toxic effects might follow absorption from fillings. The amount of arsenic in a single tooth is too small to be measured conveniently by normal analytical methods. Radioactivation analysis was used by Nixon[27] on 26 sound permanent teeth and 50 extracted teeth previously filled with zinc phosphate cements. A tissue sample of about 20 mg was taken from each tooth in a region close to the filled cavity. After irradiation in the Harwell reactor the samples were treated chemically for the isolation of arsenic.

The mean arsenic concentrations were:

normal teeth 0·060 parts/million As element

filled teeth 0·065 parts/million As element

It may be concluded that no appreciable amount of arsenic is absorbed from impurities in the filling material.

Mercury in teeth

Nixon[27] has indicated another investigation in which radioactivation analysis will be of advantage. Mercury amalgam, once believed to be a dangerous material for the filling of teeth is now generally considered

harmless, but misgivings are still expressed[28] about its possible toxicity—not unreasonably, since the amount of mercury in a typical filling is large compared with the normal daily intake of this element.

Tracer experiments have been made on extracted teeth but are clearly objectionable in living subjects. Radioactivation analysis using ^{197m}Hg ($t_{\frac{1}{2}} = 23$ h) which can be made at very high specific activity would provide the desired information without much difficulty. Particular attention should be given to the possibility of mercury absorption in children, where the greater patency of the dentinal tubules provides a more ready path for transfer than in adults.

Manganese and bone formation

Manganese is now known to be an essential trace element in many plants, but its place in human nutrition remains obscure. The concentrations normally present are so low as to be beyond the reach of conventional analytical methods. Consequently the reported values are too meagre or too discordant to be of much value. *In vitro* experiments show that several enzymes, including bone phosphatase, are activated by manganese. Dietary deficiency of this element prevents normal bone formation in rabbits, rats and mice. The resulting deformities are accompanied, in rabbits, by a pronounced depression of bone phosphatase activity.

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Dietary deficiency of this element is the cause of perosis, a serious bone disease in poultry. The disease is accompanied (and, in fact, preceded) by a marked depression of blood and bone phosphatase activity. It has been suggested[29] that slipped epiphysis, a deformity sometimes found in children, may be related to perosis. There is no evidence that manganese is essential for human nutrition. It is, however, so important to plants and animals that further study with the refined analytical methods now available is desirable. Detection by radioactivation in tissue samples is difficult because of the longer-lived and more abundant activities contributed by sodium and potassium. This problem has been tackled successfully by Borg[30] and Bowen[31].

COMBINATION OF RADIOACTIVATION WITH OTHER TECHNIQUES

The usefulness of isotopic tracers can be significantly enhanced by combination with radioactivation analysis. A small dose of a radioactive nuclide, administered to a patient or an animal, may often be used to establish the size of the exchangeable reserve of the corresponding stable element. Sometimes it is possible to study the turnover rate of an element in a biochemical reaction. There are occasions when such tests cannot be done without giving an unjustifiably high dose of radioactivity, because no isotope of suitable half-life and specific activity is available. Unless the added radioactive tracer equilibrates quickly, measurements of its storage and excretion will not be applicable to the stable element already present in the body. On the other hand, the estimation of many stable trace elements in the body or in excreta is difficult or impossible because the conventional methods of analysis are lacking in sensitivity.

Protein-bound iodine

Some of these difficulties are encountered in the radio-iodine test used for the study of thyroid function. The rate of iodine turnover in the thyroid can be estimated by measuring the radioactivity in the protein fraction of the circulating plasma; this radioactivity is mainly due to freshly-made thyroxine and tri-iodothyronine. The significance of the turnover rate cannot be fully assessed without a knowledge of the size of the stable thyroxine pool. Measurement of this quantity by estimating the ^{127}I in the plasma proteins is a task of remarkable difficulty. The concentrations to be measured are about 5 μg/100 ml of plasma in the human subject. At these levels fortuitous contamination is hard to avoid.

The estimation of protein-bound ^{127}I by radioactivation is an attractive technique which does not appear to be widely known, though it is mentioned in a recent report from Oak Ridge[32]. Proximity to a nuclear reactor is essential, since ^{128}I has a half-life of only 25 min. In Britain, and perhaps in other countries, a postal service for the estimation of protein-bound ^{127}I by radioactivation would be fully occupied and would be generally preferred to the present chemical methods.

Strontium in human bone

Strontium is another element whose behaviour can be elucidated more fully by radioactivation than by tracer tests. Here the commonly available radioactive isotopes are too dangerous for administration to human subjects at the levels needed for tracer tests. The stable element is, however, present in human and animal tissues in amounts suitable for estimation by radioactivation[33] using the short-lived $^{87}Sr(t_{\frac{1}{2}} = 2{\cdot}7$ h).

Activation chromatography

The combination of radioactivation and chromatography has been reviewed recently by Benson[34]. Many elements can be estimated rapidly and accurately by neutron irradiation of paper chromatograms, followed by inspection with a Geiger counter. Since no chemical manipulation is needed after the neutron activation, short-lived isotopes can be used. Benson measured cobalt and vanadium in tissue ash, from the activities of $^{60m}Co(t_{\frac{1}{2}} = 11$ min) and ^{52}V ($t_{\frac{1}{2}} = 3{\cdot}8$ min) on activated chromatograms. He also describes methods for the analysis of phosphorus-containing intermediates in carbohydrate and lipid metabolism. Such investigations would otherwise be very difficult in large animals, where it is not practicable to administer ^{32}P in sufficient quantities for the analysis of phosphatides by the normal methods of radiochromatography.

SCOPE OF ACTIVATION ANALYSIS

Except for a few elements at either end of the periodic table, the technique of activation analysis is almost universally applicable. Its ultimate sensitivity is usually far beyond the level required in practice. Figures published by the Oak Ridge laboratory of the United States Atomic Energy Commission[32] show the concentrations of several elements found in biological material examined there, along with the corresponding limits of

sensitivity attainable with no great difficulty in that laboratory. Even these figures, which are given in *Table 3*, can be improved by a factor of 10 or more by using a more powerful reactor or more delicate methods of radioactive assay. Many other elements, not shown in this compilation, could be studied by activation analysis if the need arose and the necessary modest effort was applied.

Table 3. Radioactivation analysis of tissue[32]

Element	*Concentrations observed in tissue* (parts/million)	*Limit of sensitivity* (parts/million)
Antimony	0·5–10	0·005
Arsenic	0·005–1	0·001
Bromine	1–10	0·001
Cadmium	1–5	0·01
Caesium	1–10	0·05
Cobalt	0·1–1	0·05
Copper	0·1–700	0·01
Iodine	1–10	0·05
Nickel	0·5–2	0·1
Potassium	100–1000	0·02
Rubidium	10–100	0·1
Selenium	0·001–10	0·001
Silver	0·1–1	0·1
Sodium	10–10,000	0·007
Strontium	6·5–30	0·5
Tellurium	10–100	0·2
Zinc	1–1000	0·02
Zirconium	1–10	0·2

Sources for radioactivation

The nuclear reactor is the most convenient instrument for radioactivation of biological material, but other possibilities have been discussed[1]. Charged particles from high-energy accelerators have a limited usefulness because of their short range and consequent intense heating effect. For some elements, including phosphorus and iron, radioactivation analysis with charged particles has very good sensitivity[35].

The electron linear accelerator, when supplied with a suitable target and moderator, makes a good neutron source. MacGregor[36] estimates a total neutron production of 3×10^{13} neutrons sec^{-1} from a 20 MeV, 12 kW electron linear accelerator operated with a water-moderated uranium target. The corresponding thermal neutron flux is 2×10^{11} neutrons cm^{-2} sec^{-1}. A linear accelerator working at 25 MeV, 10 kW will make millicurie amounts of about fifty isotopes, using (γ,n) reactions. Many of these isotopes are not available from a nuclear reactor.

Electron linear accelerators are likely to be used to an increasing extent in radiation therapy. Their possibilities for radioactivation analysis for medical purposes should not be overlooked.

When radioactive isotopes were first made by artificial means, it was often predicted that they would be widely useful in the treatment of diseases which had so far resisted the skill of the physician. These hopes have not been fully consummated, but it is becoming evident that the subtler

applications of induced radioactivity will be a fruitful field of study for practitioners of medicine and the sciences ancillary to it. Like the thermometer, the spectroscope and the oscillograph, the Geiger counter may almost be as useful in the relief of suffering as in the advancement of knowledge. In this process the technique of radioactivation analysis has a modest but distinctive contribution to offer.

In the preparation of this review I have received much information and other help from Dr Hamilton Smith. I am grateful also to Dr A. T. Doig, Dr G. S. Nixon and Dr E. Rentoul for useful discussions on many topics.

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DISCUSSION

G. W. Leddicotte (*U.S.A.*): I should like to refer to some routine analyses which I and my collaborators have carried out. In 1953, we demonstrated the presence of at least ten of the rare earths in a specimen of bone. The analysis was not carried further because of the difficulty in differentiating one type of rare earth from another. At the time, it was considered that a procedure devised by Boyd *et al.* was the most suitable for rare earth analysis and a paper on the subject was included in the *Journal of Physical Chemistry* in 1953. The technique, unfortunately, took some 72 h, during which period some of the sensitivity was lost. Nevertheless, in a sample of a hard tissue such as bone, it was possible to determine erbium, for example, in the 10^{-10} g range. The largest concentration of any rare earth in the system was 2·2 parts/million. Rare earths were also prominent in monazite ores and sands. Hickory leaves contained a few hundred parts/million of the rare earths and variations in the leaves were more or less related to monazites in various parts of North Carolina. Some of the trees were more selective for rare earths.

It was found feasible to make an analysis of cadmium in bone and a content of about 0·1 parts/million was determined. It was also feasible to determine 1 part/million of iodine during work on proteins.

Marked differences in the selenium content of human bodies as between the Dakotas and other parts of the United States have been discovered. The effects on liver tissues of the presence or absence of selenium in diets is being studied at Washington, and radioactivation analysis techniques are proving extremely important in that work.

J. H. MÜLLER (*Switzerland*): I should like to refer to work done with the object of evolving a procedure suitable for routine assessments of gold deposits in tissue specimens when ^{198}Au is used in larger doses for cancer therapy*.

The intracavity interstitial injections of radioactive colloids, especially colloidal ^{198}Au, are now of internationally acknowledged importance in cancer therapy. The essential advantages are the good anatomical localization of innumerable small radioactive foci dispersed within the required sites, together with the induction of vital reactive, mainly histiocytic phenomena, of which the most remarkable is the resulting concentration of the radioactive colloidal material within the whole tributary lymphatic apparatus of the region treated. This is of paramount importance in view of the frequent and dangerous lymphatic disseminations of the cancer cells. These therapeutic methods might be described as paraselective and, as such, within the realm of the scientific ideal of selectivity.

Qualitative data and quantitative approximations about the concentrations of radioactive particles within the lymphnodes and other anatomical structures could previously be obtained by the physical means available, *i.e.*, external counting and scanning, counting of ashed active samples, calculations and autoradiography. If there is sufficient residual activity, autoradiography provides very important evidence, but it is not adequate for making precise assessments of radiation dosage.

When colloidal ^{198}Au is used for clinical and therapeutic applications it is very difficult to work on active samples because, by the time the samples are available, the residual activity is usually minimal or has already decayed to zero. Neutron activation analysis was accordingly employed for the first time a few years ago and has yielded quantitative data of sufficient accuracy. The particular problems involved do not require extremely high precision; it is sufficient to have well-ascertained orders of magnitude which permit a reliable survey of the radiation dosimetry involved. Chemical separation is unnecessary, so that it is also possible to repeat the activation analysis—a factor of advantage in certain cases. Quantitative assessment of the gold content in samples examined is obtained solely by nuclear physical methods. Well-defined small samples of the tissues to be examined are collected—by surgery or, in exceptional cases, during autopsy—some weeks or months after ^{198}Au treatment. After the primary activity has decayed, the samples are ashed and reactivated—formerly in the B.E.P.O. reactor at Harwell, and more recently in the swimming-pool reactor at Wüzenlingen, Switzerland—together with exactly calibrated gold samples, at a site where the neutron flux is homogeneous.

* *See* J. H. Muller: "Neutron activation analysis for medical isotope dosimetry with special consideration of colloidal Au^{198}", *Radioisotopes Sci. Research, Proc. Intern. Conf., Paris, Sept., 1957*, Vol. III, pp. 667–683; Pergamon Press (1958).

For the quantitative determination of the gold content of the samples we have hitherto mostly worked from the complex decay curves obtained by scintillation counting of the reactivated samples.

Gamma scintillation spectrometry is also being used now. It is more practical as it permits a rapid and reliable survey of numerous specimens within a relatively short time. For preliminary studies we were kindly loaned a 50-channel analyser belonging to Reactor Ltd., Wüzenlingen. The procedure will soon become routine in our own laboratory where a single-channel discriminator, quite adequate for this particular work, will be used.

Results to date indicate that the definition of the average beta radiation dosage within the structures investigated is sufficiently precise. The mean values are, for example, 7000 rads within the abdominal and mediastinal lymphnodes, after intraperitoneal application of 150 mc of colloidal ^{198}Au, and 8000–16,000 rads within the axillary lymphnodes after extended colloidal ^{198}Au infiltration of the whole breast region in cases of breast cancer, performed two to three weeks before operation. For the procedure, the colloidal ^{198}Au is used in amounts of 90–130 mc diluted in 120–180 ml of physiological saline for multiple interstitial injections, aiming at a diffuse imbibition of the whole mammary, para-mammary and retro-mammary regions from the sternum to the axilla. The procedure results in gamma irradiation throughout the large area infiltrated. It is of the same order of magnitude as in conventional pre-operative Roentgen therapy but, in addition, considerable amounts of radioactive material are concentrated within the retrosternal, the axillary and even the supraclavicular lymphnodes.

I started this method of pre-operative interstitial irradiation of breast cancer some six years ago. It has given extremely encouraging preliminary clinical results and is now being used on a steadily increasing scale.

W. W. Meinke (*U.S.A.*): Our group has also been interested in analysing marine biological ashes. Dr R. Fukai of the Tokai Regional Fisheries Laboratory in Tokio has assisted in this work and a review of trace analyses in seaweed, molluscs, crustacea, fish and sea-water will be published*. This report also contains comparisons of the sensitivity of activation analysis with that of conventional methods. *Figure 2* shows this relation of sensitivities expressed in terms of the sensitivity index, pS(= −log (sensitivity in g)).

In experimental work on these samples using the Michigan reactor ^{52}V ($t_{\frac{1}{2}} = 3{\cdot}8$ min), ^{188m}Re($t_{\frac{1}{2}} = 20$ min), and ^{101}Tc($t_{\frac{1}{2}} = 14$ min) (from ^{101}Mo) have been separated by rapid radiochemical procedures and their spectra measured. Longer-lived radioisotopes of gold, arsenic and tungsten have also been determined. The approximate experimental sensitivities determined for these elements at a flux of 10^{12} neutrons cm^{-2} sec^{-1} are as follows:

Vanadium	^{52}V	2×10^{-9} g
Arsenic	^{76}As	5×10^{-8} g
Molybdenum	^{101}Tc	5×10^{-7} g
Tungsten	^{187}W	5×10^{-9} g
Rhenium	^{186}Re	1×10^{-9} g
Gold	^{198}Au	5×10^{-10} g

* *Limnology and Oceanography*, **4**, 4, 398 (1959).

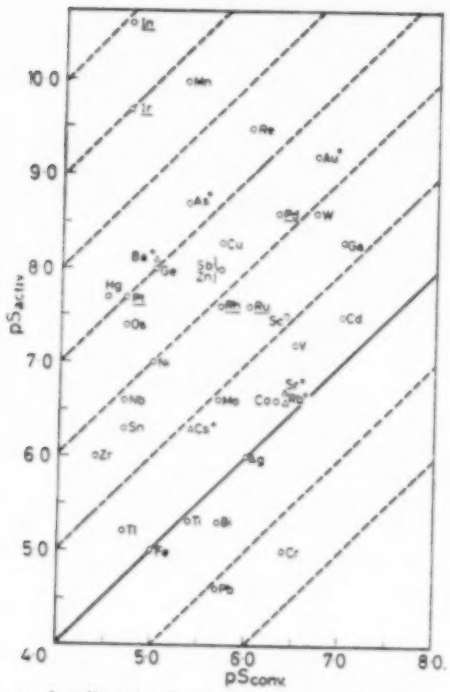

Figure 2. Comparison of radioactivation analysis sensitivity with that obtained in conventional methods. Elements whose symbols are underlined have not previously been reported in samples of the types mentioned. Activation analysis has been reported for those marked with an asterisk

The abundance of the elements in the samples in most cases did not approach these sensitivities. A short preliminary summary of the analyses has recently been submitted to *Nature**. Work has also been done by Dr D. Kaiser on the determination of cobalt in rat kidney tissues after injection of vitamin B_{12}. A rapid chemical separation isolates $^{60m}Co(t_{\frac{1}{2}} = 10{\cdot}5$ min), giving a sensitivity of about 5×10^{-8} g†. An extension of this has been a similar determination of copper in rat kidney tissue at the 10^{-6} to 10^{-7} g level by using a rapid chemical procedure and measuring $^{66}Cu(t_{\frac{1}{2}} = 5$ min).

A compendium of radiochemical information entitled *Source Material for Radiochemistry* is now available free of charge from the Division of Physical Sciences, National Research Council, 2101 Constitution Avenue, Washington 25, D.C. It contains several hundred items and lists the authors and titles of source documents, a brief abstract, address where the item is obtainable and its price.

L. C. KELLERSOHN (*France*): I agree with Dr Lenihan that the use of a tracer such as iodine-131 does not provide a complete picture of the thyroid function; it is also necessary to know the iodine-127 content of the blood, especially the plasmatic protein iodine. The chemical determination of blood iodine is complex, delicate and inclined to be imprecise.

* R. Fukai and W. W. Meinke *Nature* **184**, 815 (1959).
† D. G. Kaiser and W. W. Meinke, *Talanta* **3**, 255 (1960).

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RADIOACTIVATION ANALYSIS IN BIOCHEMISTRY AND MEDICINE

In the Frédéric-Joliot Section, Biological Service, French Atomic Energy Commissariat, we have recently attempted to devise an activation analysis dosage technique for plasmatic protein iodine. The elements which cause difficulty are mainly sodium, chlorine and bromine. But these elements do not occur in the blood organically bound. We have therefore tried to separate the blood protein iodine and mineral iodine before or after irradiation by passing them several times over ion-exchange resins or by precipitation of the protein and repeated washing. Irradiation was carried out for one hour at 2×10^{11} neutrons cm^{-2} sec^{-1}. Measurements on the samples and the standards were made by means of a 100-channel, magnetic memory analyser. The 428 keV spectrum of iodine-128 has been obtained in the sample but it does not permit precise quantitative measurement. It is hoped to reduce the Compton continuum from the spectra of sodium, chlorine and bromine by using an NaI (Tl) and anthracene crystal double-counting head.

P. LEVEQUE (*France*): In France monoenergetic photons from a 124 MeV betatron have been used for determining nitrogen, oxygen and carbon by the (γ,n) reaction. It has not proved possible to determine trace quantities of these elements. For the determination of larger quantities, however, the method is perfectly satisfactory. There is the additional advantage that the reactions are threshold. On the betatron, it has been possible to vary the maximum energy so that nitrogen (threshold 11 MeV), oxygen (threshold 16 MeV), and carbon (threshold 19 MeV) could be determined successively.

J. H. MÜLLER (*Switzerland*): Similar work has been done with a 31 MeV betatron at Zurich.

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ACTIVATION ANALYSIS OF MINOR CONSTITUENTS IN HIGH ALLOY STEELS

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L'auteur montre que l'analyse par activation n'est pas uniquement un moyen précieux pour la détermination d'éléments à l'état de traces, mais qu'elle permet aussi de déterminer la concentration d'éléments entrant pour une faible proportion dans la constitution de substances très complexes.

Les résultats obtenus sur des échantillons d'aciers spéciaux du National Bureau of Standards contenant du vanadium et du tungstène à une concentration allant de 0,01 à quelques pour cent indiquent que l'exactitude et la précision de cette méthode sont équivalentes, sinon supérieures, à celles de l'analyse chimique, même si l'on n'a pas effectué de séparation chimique préalable. L'auteur examine en détail une méthode employant un étalon interne qui permet de corriger avec précision les irrégularités du flux de neutrons entre l'échantillon et l'acier témoin.

Most authors have, until now, rightly stressed the importance of activation analysis as one of the most sensitive analytical tools for the determination of a large number of elements.

In our opinion, however, activation analysis is not only useful for the analysis of traces, but also for the determination of minor constituents in complex materials.

For elements occuring in concentrations of 0·01 per cent up to a few per cent, activation analysis can compete favourably with classical electrochemical or optical methods, as far as speed and accuracy are concerned. In most cases the latter methods will indeed require either a quantitative separation prior to the determination of the constituent to be analysed, or the removal of interfering substances, as the number of really specific reactions is rather limited. Such preliminary treatment of the sample can give rise to considerable errors and is often time-consuming.

It is obvious that this cause of errors can usually be avoided by activation analysis. After irradiation, a suitable amount of inactive carrier can be added to the sample, and a quantitative separation is not required if the yield is computed. Moreover, in many cases a separation is not even necessary as interference from other radioactive species can be avoided or corrected for. In the case of gamma emitters, for instance, the use of a single or multichannel analyser often allows selective measurement in the presence of other gamma radiations of different energy, while analysis of composite decay curves sometimes offers a means of accounting for interfering activities.

ACCURACY OF ACTIVATION ANALYSIS

It is obvious that in most cases involving activation analysis of minor constituents, errors due to poor counting statistics will usually be small,

as the concentration ranges involved are several orders of magnitude larger than in trace analysis. They will not be discussed in this place.

An important source of errors can, however, be due to differences in neutron flux between sample and reference. The content of a sample is indeed usually computed from the ratio of the activities of the sample and of a known amount of standard, rather than by absolute disintegration rates. These differences in neutron flux are mainly to be attributed to two causes: neutron flux irregularities between sample and reference, as they obviously cannot occupy the same place, and different self-shielding effects if absorption cross-sections of sample and reference are substantially different.

To correct for these differences we have developed a method of activation analysis using an internal standard[1].

Instead of irradiating a known amount of the element as a reference, two quantities a and b of the sample are irradiated, an amount c of the element X to be determined being mixed homogeneously with b. The material subjected to analysis should contain at least one element Y, which gives rise to an isotope measurable with good accuracy and having a half-life long in comparison with that of the isotope of the analysed species.

When both samples are measured at a time t after the complete decay of the species due to X, the ratio of the activities due to Y will be given by

$$\frac{A_{t(Y)}}{A'_{t(Y)}} = \left(\frac{a}{b}\right)\alpha$$

α being a correction factor which compensates for any difference in the neutron flux received by the two samples and/or for a different neutron shadowing.

By analysis of the decay curves, the activities $A_{t_0(X)}$ and $A'_{t_0(X)}$, due to the element X, can be computed at the end of the irradiation time t_0.

The specific activity of the sample, due to X, will be given by

$$S_{t_0(X)} = \frac{1}{c}\left[A'_{t_0(X)}\,\alpha - \frac{b}{a}A_{t_0(X)}\right]$$

and the percentage of X present by

$$\frac{A_{t_0(X)} \times 100}{aS_{t_0(X)}}$$

A second source of error, which is likely to be important when determining minor constituents, will be due to (n,p) and (n,α) reactions. The cross-sections of these reactions for fast neutrons in the B.E.P.O. reactor have recently been determined by Mellish *et al.*[2] and are usually several orders of magnitude smaller than those of (n,γ) reactions with thermal neutrons. As ultimate sensitivity is not needed when determining minor constituents, these interferences can be avoided by using the irradiation facilities of the reactor reflector or even of the thermal column. At these sites the ratio of thermal to fast neutron fluxes is small and enough activity is still induced to achieve accurate counting.

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As will be illustrated later by the determination of vanadium and tungsten in National Bureau of Standards high alloy steels, the standard error on a series of determinations varies between 1 and 15 per cent. These errors appear to be of the same magnitude as those computed from the certificates of the N.B.S.

ACTIVATION ANALYSIS OF VANADIUM[3]

Natural vanadium gives rise to only one product by the (n,γ) reaction, namely ^{52}V, a β–γ emitter ($\beta = 2{\cdot}7$ MeV; $\gamma = 1{\cdot}46$ MeV) having a half-life of 3·75 min. The activation cross-section is 4·5 barns.

Since the half-life of ^{52}V is too short to permit isolation of this element after irradiation, interference by a number of steel constituents is to be expected. The radiochemical properties of the most usual constituents in high alloy steels are summarized in *Table 1*.

Table 1. Radiochemical properties of steel constituents, subject to activation by thermal neutrons

Target nuclide	*Abundance* (%)	*Activation cross-section* (barns)	(n,γ) *reaction product*	$t_{\frac{1}{2}}$	*Radiation and energy* (MeV)
^{30}Si	3·05	0·11	^{31}Si	2·62 h	β–1·47
^{31}P	100	0·23	^{32}P	14·3 d	β–1·70
^{34}S	4·2	0·26	^{35}S	87 d	β–0·16
^{36}S	0·016	0·14	^{37}S	5·0 min	β–1·6; 4·3; γ 2·7
^{50}Ti	5·34	0·14	^{51}Ti	5·8 min	β–1·9; 2·2; γ 0·32
^{51}V	100	4·5	^{52}V	3·75 min	β–2·7; γ 1·46
^{54}Cr	2·38	0·3	^{55}Cr	3·52 min	β–2·8
^{55}Mn	100	13·4	^{56}Mn	2·58 h	β–2·81; 1·04; 0·73; γ 0·82; 1·81; 2·13
^{54}Fe	5·84	0·7	^{55}Fe	3·0 y	E.C. ϵ 0·21
^{58}Fe	0·31	0·7	^{59}Fe	45·1 d	β–0·46; 0·27 γ 1·10; 1·29
^{59}Co	100	100	^{60m}Co	10·5 min	γ 0·058
			^{60}Co	5·2 y	β–0·306; γ 1·17 ; 1·33
^{58}Ni	67·7	4·2	^{59}Ni	10^5 y	E.C. ϵ 1·07
^{62}Ni	3·66	15	^{63}Ni	85 y	β–0·065
^{64}Ni	1·16	2·6	^{65}Ni	2·56 h	β–2·10; 1·10; 0·60 γ 1·49; 1·12; 0·37
^{63}Cu	69·1	4·3	^{64}Cu	12·8 h	E.C., β–0·571; β+0·66; γ 1·34
^{65}Cu	30·9	2·1	^{66}Cu	5·1 min	β–2·63; 1·59; γ 1·04
^{93}Nb	100	1·0	^{94m}Nb	6·6 min	I.T.: 0·042
^{98}Mo	23·75	0·13	^{99}Mo	67 h	β–1·23; 0·45; γ 0·04–0·78
^{100}Mo	9·62	0·20	^{101}Mo	14·6 min	β–1·2; 2·2; γ 0·191; 0·96
^{181}Ta	100	21	^{182}Ta	113 d	β–0·51; γ 0·334–1·18
^{184}W	30·6	2·1	^{185}W	73 d	β–0·43; 0·37; γ 0·058
^{186}W	28·4	34	^{187}W	23·9 h	β–0·62; 1·33; γ 0·072–0·78

It appears that if a short irradiation time is used and measurements are carried out with a single-channel analyser, restricting the counting within a band ranging from 1·3 to 1·5 MeV gamma's, the only radiations giving appreciable interference are the 1·81 and 2·13 MeV gamma's of ^{56}Mn, which produce Compton recoil pulses in this energy band.

Possible interference from ^{52}Cr and ^{55}Mn, which also give rise to ^{52}V by (n,p) or (n,α) reactions, was investigated. At a site near the reflector of the BR-1 reactor, with a Cd ratio and a neutron flux of respectively

280 and 10^{10} neutrons cm^{-2} sec^{-1}, samples of 51·7 mg of manganese, 149 mg of chromium and 13·9 mg of vanadium were irradiated during 10 sec periods and counted in a well-type scintillation detector connected to a single-channel analyser, set to measure an energy band as described above. The results are illustrated in *Figure 1*, from which it is seen that no evidence of

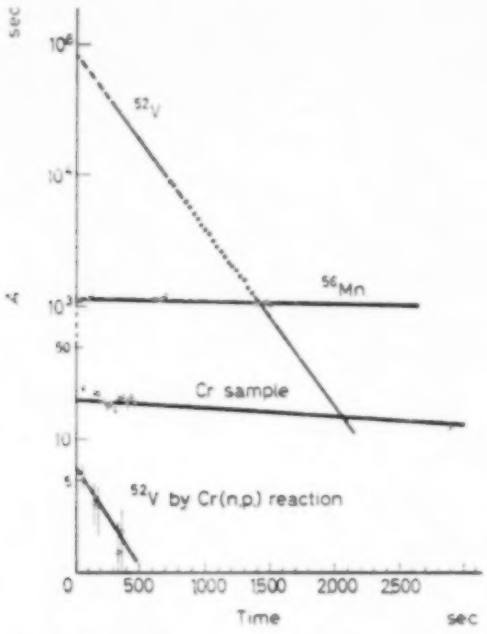

Figure 1. Interference by (n,p) and (n,α) reactions

a ^{55}Mn (n,α) ^{52}V reaction was found, whereas ^{52}V is formed to a small extent by (n,p) on ^{52}Cr. In our experimental conditions this error will be of the order of 1 per cent for a chromium/vanadium ratio of 1000/1 and consequently negligible for most practical purposes. In less favourable conditions, however, this error can become quite important. In activation analysis with the Amsterdam cyclotron, where neutrons are produced with 26 MeV deuterons on a beryllium target and thermalized in a 20 cm paraffin block, a chromium/vanadium ratio of 1000/1 would give rise to a 220 per cent error.

The internal standard procedure, described above, was tested on a number of N.B.S. high alloy steels. In most cases an irradiating facility near the reflector of the BR-1 reactor was used with a neutron flux of 10^{10} neutrons cm^{-2} sec^{-1}. The steel turnings were transferred into the neighbourhood of the counting room by means of a pneumatic tube. The samples *a* and *b* were counted alternately during 20 sec periods with a lapse of 10 sec between successive periods in a well-type detector connected to a single-channel analyser. A typical plot is shown in *Figure 2* from which

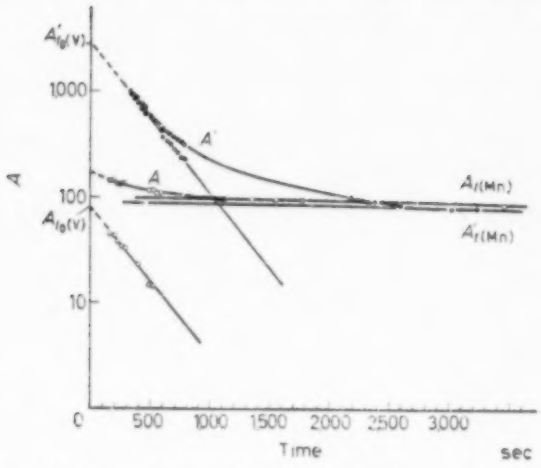

Figure 2. Determination of vanadium with internal standard

a, the neutron correction factor, as well as the vanadium activities at the time t_0 can be computed by analysis of the decay curve and extrapolation.

Results for a number of N.B.S. steels are given in *Table 2.*

The standard error on sample 155, for instance, as computed from the eight analyses given by the N.B.S. is 27 per cent, whereas it is 16 per cent on seven activation analyses. On sample 101d the standard error on ten N.B.S. analyses is 5·6 per cent, whereas the corresponding error on four activation analyses is 7·9 per cent.

It is also apparent that all the results obtained by activation analysis are in excellent agreement with those of the N.B.S.

ACTIVATION ANALYSIS OF TUNGSTEN[4]

The classical analysis of tungsten in high alloy steels presents a number of difficulties as the quantitative separation of small amounts of tungstic acid is difficult to achieve. Furthermore, the precipitate is impure due to co-precipitation or adsorption of molybdenum, vanadium, tantalum, niobium, silicon, *etc.*

These difficulties can be avoided by activation analysis, as the nuclear properties of tungsten are rather favourable. Natural tungsten gives rise to several isotopes, by the (n,γ) reaction on the natural element, of which ^{187}W, a β–γ emitter with a 24 h half-life was used for our purpose.

Two procedures were considered, namely with and without chemical separation of the tungsten as tungstic acid.

In the former case a number of radioactive species, produced by (n,γ) reaction on the other steel constituents, are likely to interfere. Short-lived isotopes, such as ^{52}V, ^{66}Cu, ^{60m}Co and ^{101}Mo will decay completely within a few hours after the end of the bombardment, while the half-life of ^{56}Mn differs sufficiently to allow correction to be made for this activity by analysis of the decay curve. The long-lived species, such as ^{51}Cr, ^{59}Fe, ^{182}Ta and

Table 2. Activation analysis results for some N.B.S. steels

N.B.S. standard sample	V (%)	Mn (%)	Cr (%)	W (%)	Ni (%)	*Sample weight* (mg) *a*	*b*	*c*	*Correction factor*	$A_{t_0(V)}$ (counts/sec)	$A'_{t_0(V)}$ (counts/sec)	V (%) *found by activation analysis*	*Standard error* (%)
155* Cr–W steel	0·014	1·24	0·485	0·517	0·100	296·7	447·2	3·236	1·062	24·5	1,516	0·0170	
						604·5	610·4	5·942	1·046	28·4	2,510	0·011	
						600·3	824·4	9·806	0·979	3·5	384·0	$0·017_4$	
						642·9	654·9	8·605	1·062	29	2,130	$0·017_4$	15·8
						657·5	548·8	15·077	1·079	3·65	578	$0·013_4$	
						527·3	649·3	13·684	1·044	4·7	840	0·014	
						661·4	793·6	8·470	1·028	26·4	1,920	$0·017_4$	
												$\bar{m} = 0·015_3 \pm 0·0024$	
161* Ni–Cr casting alloy	0·029	1·28	16·88	—	64·29	336·8	132·3	2·190	0·9023	55	1,620	0·025	
						397·4	363·9	5·358	1·108	87	3,800	$0·028_5$	10·2
						332·7	504·3	3·620	1·063	19·2	680	0·030	
						472·7	412·3	7·490	0·961	64·8	3,400	0·032	
												$\bar{m} = 0·029 \pm 0·0029$	
101d* Cr–Ni steel	0·049	0·739	18·68	—	9·05	36,198	403·6	6·998	1·236	82	2,868	0·046	
						193·3	205·9	1·521	1·074	76	1,316	0·045	7·9
						223·8	239·7	5·273	1·007	62·5	3,122	0·048	
						221·5	386·9	3·877	1·059	47·5	1,530	0·054	
												$\bar{m} = 0·048_3 \pm 0·038$	
153† Co–Mo–W steel	2·04	0·219	4·14	1·58	0·107	1,137·3	937·2	26·28	0·995	66·2	133·60	1·95	
						640·6	474·3	21·74	0·882	44·0	115·20	2·16	
						640·8	634·2	11·95	0·985	63·2	129·60	1·81	
												$\bar{m} = 1·97 \pm 0·17$	

* 10 sec irradiation in BR-1 reactor, neutron flux: 10^{9}–10^{10} neutrons cm^{-2} sec^{-1}; Cd ratio: 280.
† 60 sec irradiation with Amsterdam cyclotron, neutron flux: 10^{7} neutrons cm^{-2} sec^{-1}; Cd radio: 7.

^{60}Co can also be easily distinguished from ^{187}W. The half-lives of ^{64}Cu, ^{76}As and ^{99}Mo are, however, similar to that of ^{187}W and will cause interference if certain limiting proportions are exceeded. The interference (per cent) for definite ratios as a function of time is given in *Figure 3*.

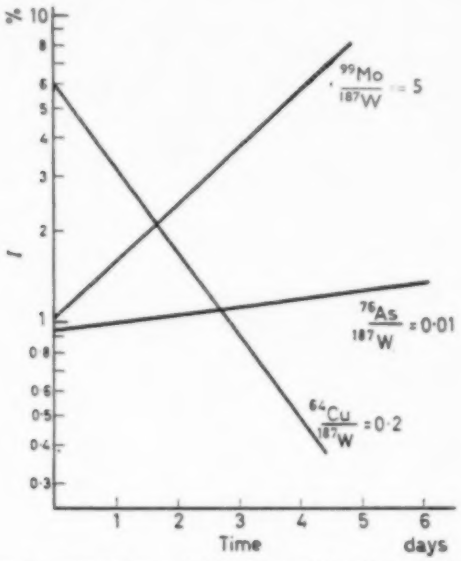

Figure 3. Interfering activities due to ^{64}Cu, ^{76}As and ^{99}Mo

Typical decay curves for two steel samples are given in *Figure 4*.

As the cross-sections of tungsten and of some cobalt steels are quite high, self-shielding effects are far from negligible, as illustrated in *Figure 5*, where the specific activity is measured as a function of sample size.

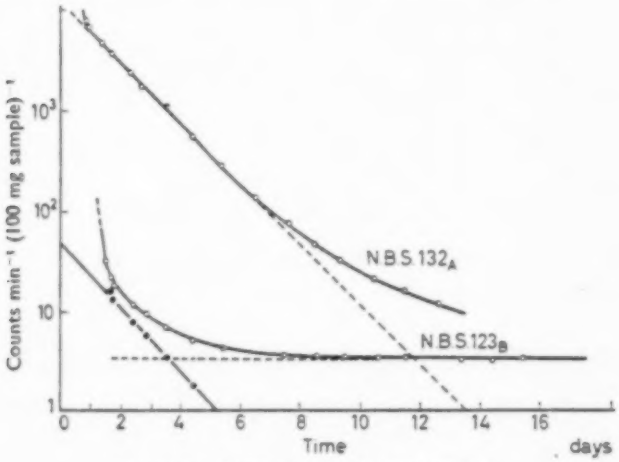

Figure 4. Decay of activated steel samples

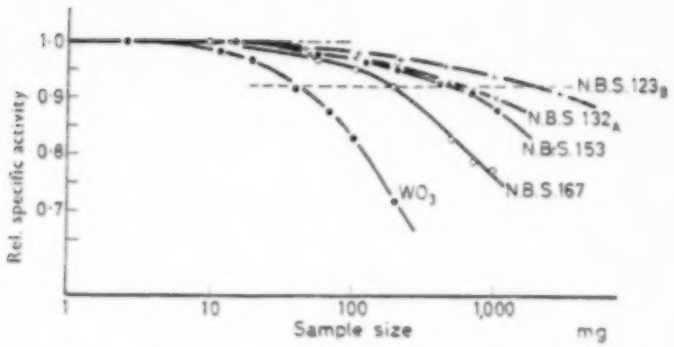

Figure 5. Influence of sample size on the neutron self-shielding

It appears that samples should be kept quite small if errors due to self-shielding are to be avoided. To obviate this, use was made of the internal standard procedure. The total activities of the long-lived species were used to compute α, the neutron correction factor. A typical example is illustrated in *Figure 6*, whereas results on a number of N.B.S. steels are represented in *Table 3*.

It appears from *Table 3* that the results are in good agreement with those of the N.B.S. and that the mean error is of the same order of magnitude.

The method without chemical separation has, however, the disadvantage that accurate results cannot be obtained if larger amounts of copper, arsenic and molybdenum are present than those indicated above. Furthermore, results are only available after about fifteen days, as graphical analysis of the decay curves are necessary.

It is possible to avoid these disadvantages by separating tungsten as tungstic acid after addition of a suitable amount of tungsten carrier. Double homogeneous precipitation of tungstic acid from perchloric acid and hydrogen peroxide in the presence of vanadate, to reduce molybdenum

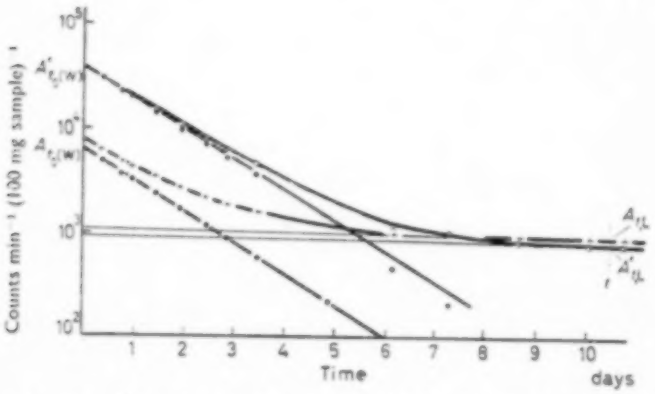

Figure 6. Determination of tungsten in N.B.S. steel 123_B by means of internal standard

adsorption, ensures a tungsten recovery better than 99·8 per cent and gives a sufficient radiochemical purification from most of the steel constituents, except tantalum. Results of the analysis of a number of N.B.S. steels are summarized in *Table 4*.

Table 3. Activation analysis for tungsten without chemical separation

N.B.S. steel	*N.B.S. results*	*Mean error*	*Sample size* (mg)	W (%)	*Mean value*	*Mean error*
132_A	6·20	0·07	510·9	6·07	6·14*	0·08
			506·4	6·13		
			601·9	6·15		
			601·2	6·05		
			603·4	6·21		
			614·6	6·25		
			22·272	6·24		
			22·484	6·25	6·20†	0·045
			18·363	6·20		
			17·748	6·11		
167	4·5	provis. certif.	190·0	4·25	4·30*	0·05
			190·0	4·30		
			11·082	4·39		
			14·174	4·41	4·40†	0·020
			13·230	4·42		
			20·284	4·37		
153	1·58	0·027	506·4	1·58		
			501·2	1·59	1·59*	0·01
			17·672	1·61		
			32·379	1·56	1·60†	0·02
			23·084	1·60		
			28·259	1·62		
155	0·517	0·006	1,055·9	0·516		
			1,092·9	0·512	0·514*	0·01
			66·851	0·527		
			68·547	0·528	0·520†	0·007
			34·519	0·508		
				0·518		
125_B	0·18	provis. certif.	2,122·0	0·191	0·20*	0·02
			2,009·6	0·209		

* Cyclotron activation.
† BR-1 reactor activation.

Table 4. Activation analysis for tungsten, with chemical separation

N.B.S. steel	*N.B.S. results*	*Mean error*	*Sample size* (mg)	W (%)	*Mean value*	*Mean error*
132_A	6·20	0·07	491·4 507·0 596·7 598·5	6·17 6·28 6·25 6·22	6·23*	0·04
155	0·517	0·006	4008·1 1067·6	0·52 0·52	0·52†*	0·001
167	4·5	provis. certif.	190·5 190·0	4·17 4·25	4·21*	0·04
			5·075 5·382 9·816	4·30 4·26 4·35	4·30†	0·03
153	1·58	0·027	467·6 518·1	1·60 1·60	1·60*	0·01
123_B	0·18	provis. certif.	1967·8 2085·5	0·170 0·172	0·171*	0·001

* Cyclotron irradiation.
† BR-1 reactor irradiation.

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DISCUSSION

D. Gibbons (*U.K.*): What procedure is used to ensure that the amount of impurity added to the reference sample is homogeneously dispersed so that it receives the same neutron flux as the impurity already present? If the internal standard method corrects for varying neutron fluxes and self-shielding effects, why is the precision of the tungsten results higher for smaller samples, in which the self-shielding effect is smaller?

J. Hoste (*Belgium*): The vanadium was added to the finely divided steel turnings in the form of ammonium vanadate, which adhered satisfactorily; similarly, the tungsten was added as tungsten oxide.

With regard to Dr Gibbons's second question, some of the analyses were carried out, before the BR-1 reactor was in operation, on the cyclotron at Louvain at a neutron flux of only 10^7 neutrons cm^{-2} sec^{-1}.

P. Leveque (*France*): How do you construct your decay curves from the experimental plots? Some people prefer to trace a straight line at a mean distance from the plots, while others prefer the least square method.

J. Hoste (*Belgium*): I have used the former method, but in the case of tungsten the direction of slope was made to fit the half-life of tungsten (24 h).

W. W. Meinke (*U.S.A.*): I should like your comments on the accuracies of the results quoted in your paper, which are in many cases more precise than those of the chemical analyses given in the N.B.S. standards.

J. Hoste (*Belgium*): It is difficult to distinguish between accuracy and precision in chemical analysis. I assumed that the N.B.S. standards were accurate and computed the standard error from about ten analyses given for one steel. Subsequently I performed radioactivation analysis and computed the standard error, which was in many cases smaller than the error from the N.B.S. standards. The results are therefore more precise without necessarily being more accurate.

G. W. Reed (*U.S.A*): May I propose that we discuss further this matter of accuracy? In particular I should like to hear what types of systematic errors are considered by workers applying these techniques.

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J. Hoste (*Belgium*): I agree. I have found it very difficult to obtain accurate standards for emission spectroscopy work on alloys.

D. Mapper (*U.K.*): Dr Reed has stated an important problem in activation analysis. In our work on the determination of copper, nickel, and cobalt in geochemical materials, we extended the work to a study of standard (B.C.S.) steels. Although the content of these three elements is higher in these steels than one desires in trace element analysis, it is very difficult to obtain materials with accurately known trace content. We found that though the nickel and copper results were in excellent agreement, some of the cobalt results were quite different from those reported. Further investigation by B.C.S. showed that the previously published cobalt determinations were in error.

In our germanium work, too, we have obtained excellent agreement with the results by other methods, and those reported by different workers.

It would be of great help to chemists in the field of activation analysis, to be able to obtain standard samples, which have an accurately known trace element content.

G. W. Leddicotte (*U.S.A.*): I agree with Dr Hoste's suggestion that internal standards should be used. Since the absolute disintegration rate of cobalt-60 may be determined, a cobalt monitor would serve as a good internal standard.

With regard to the size of samples, I think that small samples must be used in all cases except where the flux is very low. Our experience in the determination of sulphur (about 10 parts/million) in chromium by the (n,p) reaction has shown that the results vary by a factor of five when the sample size varies from 100 mg to several grams. While the neutron flux is fairly homogeneous in a graphite reactor, there may be quite pronounced variations of flux in other types of reactor. Again, a cobalt monitor or some other comparative sample technique would solve the problem.

G. LELIAERT (*Belgium*): The use of ^{60}Co as a monitor is not always feasible as there is also a time dependence, quite apart from variations in the neutron flux. I think that a monitor should be used in which the radioisotope produced has a half-life comparable with that of the radioisotope under examination.

G. W. REED (*U.S.A.*): I should like to say a word of warning about using internal standards. Using a nuclide, different from that being measured, to monitor an irradiation is probably quite satisfactory in a uniform thermal flux as found in the thermal columns of some reactors. However, many reactors today are water boilers, swimming pools, *etc.*, and a high percentage of the neutrons used are in the epi-thermal region. Most nuclides have resonance cross-sections, and these, coupled with high resonance fluxes, spell trouble. We feel it is necessary to construct calibration curves of activity against weight for the sought-after activity, and to make the monitor as nearly similar to the sample as possible; otherwise one cannot be sure of what is being measured.

F. GIRARDI (*Italy*): With regard to the cobalt monitoring suggested by Dr Leddicotte, I should like to add that while the nuclear constants of cobalt are generally well known, the resonance integral of cobalt, which may be important where fast fluxes are involved, is not so well known.

At Chalk River cobalt wires 1/5,000 in. thick were used and it was assumed that no self-absorption occurred; but after some experiments using highly dilute cobalt in aluminium the resonance absorption peak of cobalt was found to be mainly due to scattering. The resonance integral of cobalt changed from 48·6 to 75 barns so that a big correction had to be made on all measurements.

G. LELIAERT (*Belgium*): The complete decay curve is not always necesary in order to obtain a correction for the internal standard. One can also use a gamma spectrometer and the correction factor obtained from the ratio of the areas of the photo-peaks of the control isotope and the element under investigation.

ANALYSE SYSTÉMATIQUE DE L'ALUMINIUM ET DU FER DE "ZONE FONDUE" APRÈS IRRADIATION À LA PILE ATOMIQUE

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Radioactivation analysis has been used in studies on the preparation of metals of high purity, and on the influence of minute amounts of impurities in metals. Since only small quantities of material have been available for examination, a scheme has been developed which permits the separation of a large number of radioisotopes from one analytical sample. Examples are given of the analysis of impurities in specimens of aluminium and iron.

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Au laboratoire du Professeur Chaudron à Vitry, une part importante des recherches porte sur la préparation de métaux à un très haut degré de pureté et sur l'étude de l'influence de très faibles concentrations d'impuretés sur les propriétés physiques et chimiques de ces métaux, en particulier l'aluminium et le fer.

C'est pourquoi nous avons entrepris d'utiliser les radioisotopes pour ces études et en particulier pour déterminer la pureté de nos échantillons et suivre les différentes étapes de leur purification.

Disposant seulement de petites quantités de métal pour l'analyse, nous avons dès le début de nos essais en 1950 recherché à isoler le plus grand nombre possible de radioisotopes sur une prise d'essai. Nous voulons vous présenter le schéma des séparations chimiques que nous utilisons actuellement et vous donner quelques exemples des résultats obtenus.

CAS DE L'ALUMINIUM

Nous irradions environ 1 g de métal pendant une semaine dans EL_2 à Saclay et si nous voulons éviter la reaction (n,α) sur l'aluminium nous ne pouvons utiliser qu'un flux de 10^{12} neutrons cm^{-2} sec^{-1} environ. L'échantillon est décapé à la soude, puis dissout dans l'acide chlorhydrique contenant quelques mg de chlorure mercurique. Nous séparons alors les radioisotopes produits en grands groupes principaux par des précipitations par des réactifs simples:

(1) Hydrogène sulfuré en milieu acide chlorhydrique sur du cuivre et de l'arsenic entraîneurs. Nous séparons à ce moment l'aluminium en chlorure d'aluminium hydraté ($6H_2O$).

(2) Ammoniaque en milieu réducteur pour obtenir le chrome, puis en milieu oxydant pour précipiter le manganèse en bioxyde de manganèse sur du lanthane et du manganèse entraîneurs.

(3) Hydrogène sulfuré en milieu ammoniacal sur nickel, cobalt, zinc et cadmium entraîneurs.

* Travail effectué en collaboration avec M. J. Gaittet.

(4) Carbonate d'ammonium sur calcium et strontium entraineur.

(5) Enfin il reste en solution les éléments du groupe des alcalins, car nous poussons chaque séparation jusqu'à épuisement des ions de chaque groupe de la solution en effectuant autant de précipitations qu'il est nécéssaire (trois ou quatre, s'il le faut).

Au moment de sa séparation, chaque grand groupe chimique est pris en charge par un chercheur qui entreprend alors la séparation des radio-isotopes selon les processus que vous montre le schema de la *Figure 1.*

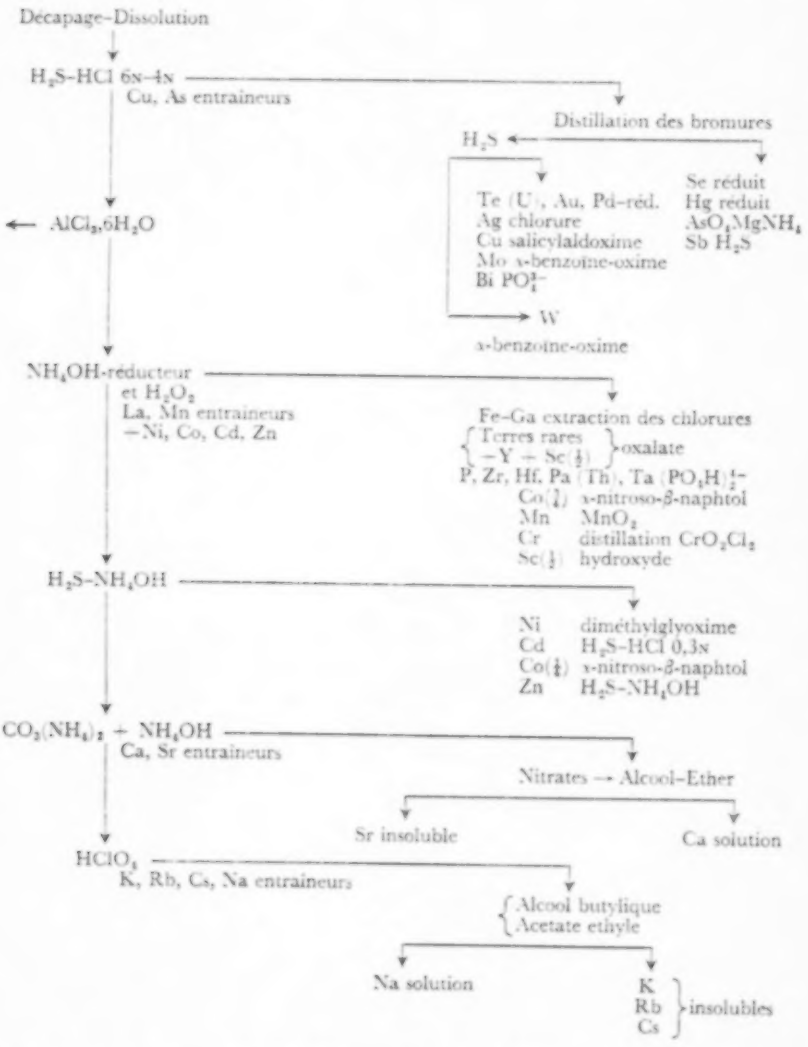

Figure 1. Analyse systématique de l'aluminium pur. Schéma des séparations chimiques effectuées pour isoler les radioisotopes produits pendant l'irradiation aux neutrons

Groupe des éléments dont les sulfures précipitent en milieu acide chlorhydrique

En général sur trois à cinq précipités successifs nous récupérons la totalité du cuivre, tellure, or, palladium, bismuth, tungstène, molybdène, sélénium, mercure, arsenic et antimoine. Une première séparation en deux sous groupe des radioisotopes de ce groupe est obtenue par distillation des bromures de sélénium, mercure, arsenic et antimoine. Dans le résidu on reprécipite en milieu acide sulfurique dilué le tellure, or, palladium, cuivre, molybdène, le bismuth par hydrogène sulfuré tandis que le tungstène reste en solution. Le tellure, l'or et le palladium sont séparés par extraction du bromure d'or par l'éther et dans la phase aqueuse on effectue la séparation de la diméthylglyoxime de palladium. Du tellure reprécipité on sépare l'iode par distillation, ce qui permet de detecter la présence, nuisible pour l'analyse, d'uranium par le ^{132}I ($t_{\frac{1}{2}} = 2{\cdot}4$ h). Après un ou deux traitements de purification de chacun des isotopes isolés on obtient des courbes de décroissances pures.

Groupe des éléments dont les hydroxydes précipitent en milieu ammoniacal

Le premier hydroxyde de " lanthane entraîneur " est précipité en milieu réducteur car nous avons constaté que le chrome est bien mieux entraîné dans ces conditions. Les deux ou trois autres hydroxydes de " lanthane + manganèse entraîneurs " sont précipités par l'eau oxygénée de façon à entraîner manganèse en bioxyde de manganèse. Ensuite sur la dissolution de ces hydroxydes nous séparons successivement:

(1) Le fer et le gallium par extraction des chlorures par l'éther. Le fer et le gallium sont séparés par traitement à la *soude*.

(2) Les terres rares et environ un tiers à une moitié du scandium et l'yttrium sous forme d'oxalates de lanthane; ensuite ce groupe est séparé par échange d'ion sur résine " Dowex 50 ".

(3) Le zirconium, le hafnium et le protactinium venant du thorium, le tantale et le phosphore qui sont précipités ensemble par les triphosphates de zirconium " entraîneur ".

(4) 75 pour cent du cobalt (ce qui est entraîné par les hydroxydes) sur une alpha-nitroso-bêta-naphtol.

(5) Le manganèse sous forme de bioxyde de manganèse en milieu acide chlorhydrique (0,1N).

(6) Le chrome et la seconde moitié du scandium sur un hydroxyde de zirconium entraîneur en milieu réducteur. Ensuite le chrome est séparé du scandium par distillation du chlorure de chromyle.

Séparation des terres rares, yttrium, scandium

C'est, croyons-nous, pour la première fois en 1950 que nous avons montré la présence de terres rares dans l'aluminium même de très haute pureté. Par l'élution, suivant le procédé de Nerwick, par le lactate d'ammonium des radioisotopes du groupe des terres rares fixées sur une résine " Dowex 50 ", nous avons pu séparer, dans un type d'aluminium raffiné par double electrolyse, dix éléments. Le *Tableau 1* montre les isotopes identifiés et les activités mesurées. Le schéma de la *Figure 2* présente dans un diagramme

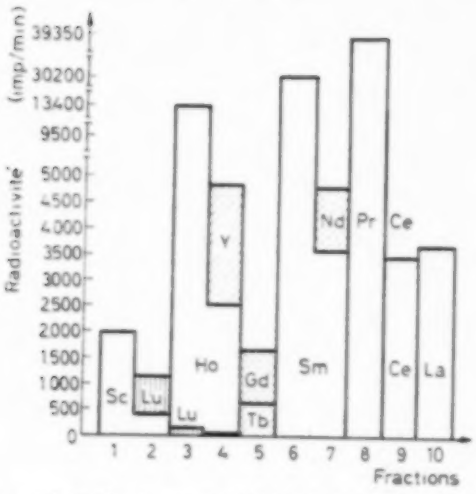

Figure 2. Diagramme schématique montrant l'ordre d'élution des éléments des terres rares détectés dans un échantillon d'aluminium de titre conventionnel 99,9992 pour cent

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plus suggestif ces résultats. Nous préciserons que l'identification du scandium dans les premières fractions éluées est très facilitée par emploi de la spectrométrie gamma (*Figure 3*). Nous mentionnerons tout de suite que ces dosages sont très importants: en effet, si le scandium est à une teneur de l'ordre de 0,5 à 1 parties/million dans l'aluminium pur industriel,

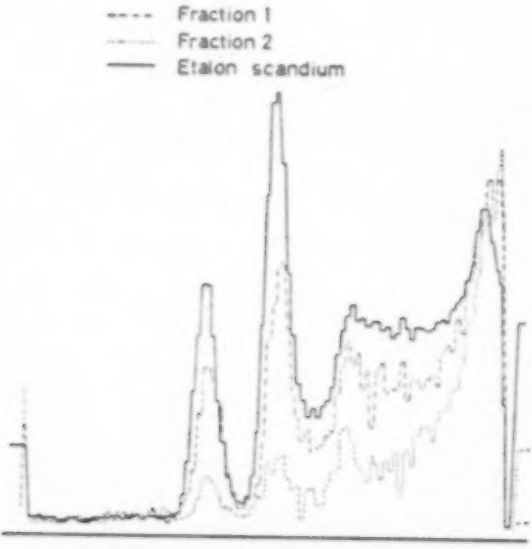

Figure 3. Comparaison des spectres du rayonnement γ des fractions 1 et 2 de l'élution des terres rares au spectre du rayonnement γ d'un étalon de scandium-46

il n'est pas éliminé par la méthode de la " zone fondue " et sa concentration dans ce métal ultra-pur est encore de 0,4 à 0,5 parties/million et il constitue alors la plus importante des impuretés dosées actuellement*.

Tableau I. Séparation, sur résine " Dowex 50 " par élution au lactate d'ammonium, des radioisotopes des éléments du groupe des terres rares, du scandium et de l'yttrium. Les isotopes sont identifiés par leur position dans l'ordre d'élution et par leur " période " de décroissance

Fractions	*Periodes*	*Activités* (imp/min)	*Isotopes trouvés*	*Elements dosés*
1	85 j	2000	^{46}Sc 85 j	Sc
2	6 j	750	^{177}Lu 6,8 j	Lu
	88 h	400	^{46}Sc 85 j	Sc
3	27 h	13200	^{166}Ho 27,3 h	Ho
	7 j	151	^{177}Lu 6,8 j	Lu
	87 j	76	^{46}Sc 85 j	Sc
4	23 h	2500	^{166}Ho 27,3 h ^{159}Gd 18 h	Ho Gd
	60 h	2240	^{90}Y 61 h	Y
	63 j	40	^{160}Tb 73,5 j	Tb
5	21 h	1000	^{159}Gd 18 h	Gd
	6-8 j	250	^{161}Tb 7 j	Gd*
	75 j	400	^{160}Tb 73,5 j	Tb
6	2-2,1 j	30200	^{153}Sm 47 h	Sm
	Très longue	10	^{151}Sm 80 a	Sm
7	47,4 h	3630	^{153}Sm 47 h ^{149}Pm 50 h	Sm Nd*
	12,2 j	1150	^{147}Nd 11,3 j	Nd
8	22 h	38000	^{143}Pr 19,2 h	Pr
	13,6 j	1350	^{143}Pr 13,7 j	Ce*
9	33,6 h	3550	^{148}Ce 33 h	Ce
	29,5 j	2240	^{141}Ce 33,1 j	Ce
10	40 h	3700	^{140}La 40 h	La

* ^{143}Ce $\xrightarrow[33\ h]{\beta^-}$ ^{143}Pr ; ^{161}Gd $\xrightarrow[3,7\ min]{\beta^-}$ ^{161}Tb ; ^{160}Nd $\xrightarrow[1,8\ h]{\beta^-}$ ^{160}Pm

Séparations du zirconium, hafnium et protactinium

Dans le sous-groupe des phosphates, nous pouvons identifier et doser le zirconium, et le thorium par le protactinium-233 en utilisant l'analyse de la radioactivité de ces isotopes par la spectrométrie gamma. Dans les aluminiums raffinés par double électrolyse et dans le métal purifié par " zone fondue ", nous ne trouvons ni ^{95}Zr ni ^{181}Hf mais, par contre, nous pouvons détecter des traces de ^{233}Pa, qui correspondent à 2×10^{-3} parties/million environ de thorium dans le métal industriel et 6 parties/million dans la partie des barreaux, traités par " zone fondue ", où s'accumulent les impuretés. Les *Figures 4* et *5* montrent les spectres du rayonnement gamma obtenus.

* Dans un échantillon d'aluminium purifié par 38 possages de " zone fondue " nous avons trouvé une teneur en scandium de 0,17 à 0,18 parties/million.

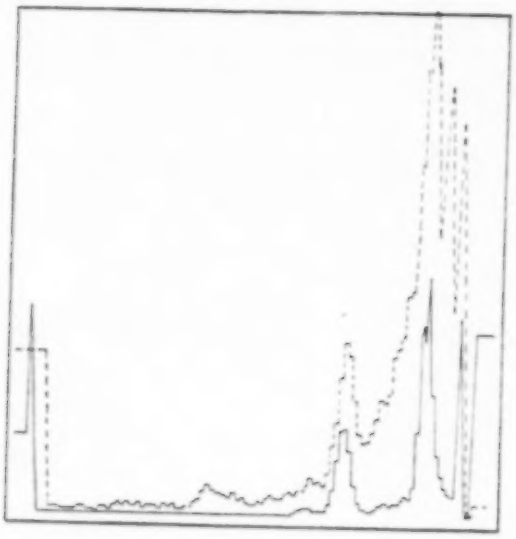

Figure 4. Analyse d'un échantillon d'aluminium raffiné de titre conventionnel 99,9992 pour cent: --- Spectre du rayonnement γ du groupe des phosphates insolubles $(PO_4H)_2Zr$ sur Al 6174 — Th: 2×10^{-9} parties/million); — spectre du rayonnement γ du protactinium-233 ($^{233}Th \xrightarrow{\beta^-} {}^{233}Pa$; Th: 3 μg)

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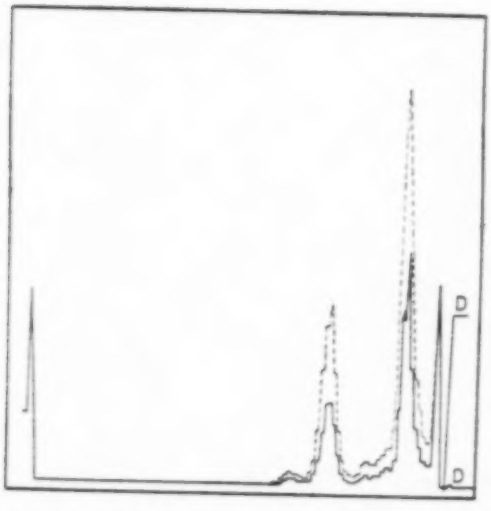

Figure 5. Analyse d'un échantillon d'aluminium prélevé en queue d'un barreau traité par "zone fondue". Comparaison du spectre du rayonnement γ du groupe des phosphates insolubles (---) et du spectre du rayonnement γ d'un étalon protoactinium 6 parties/million de thorium (—)

Autres groupes chimiques

En ce qui concerne les autres groupes, les séparations décrites dans le tableau de la *Figure 1* sont simples et ne nécessitent pas de commentaires.

Dans le groupe des alcalins nous avons isolé le sodium des éléments dont les perchlorates sont insolubles afin de séparer éventuellement le ^{42}K ($t_{\frac{1}{2}} = 12{,}4$ h) du ^{24}Na ($t_{\frac{1}{2}} = 15$ h). Le groupe des perchlorates ne contient pas de radioactivité; par contre, nous trouvons dans les aluminiums industriels de 2 à 4 parties/million de sodium. Dans l'aluminium de " zone fondue " la teneur en sodium est inférieure ou égale à 0,2 parties/million; en effet, nous ne pouvons dire encore actuellement s'il y a 0,2 parties/million " d'essai à blanc " dû à la réaction (n,α) produite par la petite fraction de neutrons rapides qui peuvent se trouver dans le flux de neutrons thermiques.

CAS DE L'ANALYSE DU FER PUR

Nous avons commencé nos essais sur le fer en ne changeant que le procédé de séparation de l'élément de base: le fer est extrait par l'éther en chlorure ferrique. Dans l'extrait à l'éther on isole le gallium par traitement à la soude et donc le premier sous-groupe du groupe des hydroxydes disparaît.

Cependant, nous avons dû changer très vite la technique d'attaque du fer car, si le fer est pur, il ne s'attaque que très lentement dans l'acide chlorhydrique.

Nous dissolvons le fer par l'acide nitrique, chassons l'excès d'acide par l'acide formique et complexons le fer par l'acide oxalique. Dans ces conditions, il y a quelques modifications nécessaires du schéma analytique de la *Figure 1*.

Le cadmium précipite par hydrogène sulfuré en milieu acide oxalique et vient prendre la place du tungstène qui, lui, ne précipite plus.

On isole alors le tungstène sur un nouveau groupe qui se place après l'extraction du chlorure ferrique à l'éther et avant la précipitation du groupe des hydroxydes. En milieu chlorhydrique 6N, on précipite le tungstène sur " entraîneurs " cuivre et arsenic par hydrogène sulfuré en trois à quatre précipitations successives.

RÉSULTATS DES ANALYSES SYSTÉMATIQUES

Le *Tableau 2* réunit à titre d'exemple les résultats de quelques analyses d'aluminium et de fer de très haute pureté.

Nous noterons que la teneur en molybdène du fer s'explique par la présence de cette impureté dans la nacelle de chaux utilisée; le fer électrolytique d'origine ne contient que 2 parties/million de molybdène. La teneur en cuivre est également anormalement élevée, actuellement nous trouvons 0,5 parties/million de cuivre environ dans le fer de " zone fondue ".

Pour l'aluminium il est important de savoir que l'aluminium dont l'analyse est réunie dans la première colonne est un métal très pur industriel raffiné par double électrolyse dont le titre conventionnel, tenant compte seulement du cuivre, fer et silicium est de 99,9992 pour cent (Fe = 3, Cu = 2, Si = 3 parties/million) alors que son titre réel est de l'ordre de 99,9950 pour cent (~50 à 60 parties/million).

Tableau 2. Résultats montrant les concentrations en impuretés trouvées dans des échantillons d'aluminium et de fer très purs. Pour un grand nombre d'éléments nous ne détectons que de très faibles radioactivités et selon les conditions expérimentales des mesures nous pouvons préciser que les concentrations d'impuretés sont $\leqslant$ ou $<$ ou $\ll$, aux valeurs numériques du tableau. Les concentrations sont exprimées en parties par million (10^{-6})

Eléments dosés	*Aluminium* 99,9992%	*Aluminium nacelle "* Al_2O_3 *"*	*" zone fondue " nacelle " graphite "*	*Fer " zone fondue "*
Selenium	$<0,1$	—	$<0,02$	$<0,02$
Mercure	$\ll 0,01$	—	$<0,004$	$\leqslant 0,01$
Arsenic	0,15	0,001	$0,001_5$	$\leqslant 0,002$
Antimoine	1,2	0,002	$0,002_6$	$\leqslant 0,002$
Cuivre	1,9	0,080	0,020	4,8
Molybdène	$\leqslant 0,2$	—	—	5.
Tungstène	$\ll 0,01$	—	—	0,03
Bismuth	$<0,1$	—	—	$<0,1$
Argent	$<0,1$	—	$\ll 0,1$	$\ll 0,1$
Or–Pd	$\ll 0,001$	$\ll 0,001$	$\ll 0,001$	$\leqslant 0,001$
Tellure	$\ll 0,1$	—	—	$<0,05$
Uranium (Tef)	0,002	—	—	$<0,002$
Fer	3.	$\ll 1$	$\ll 1$	—
Gallium	0,3	0,05	0,02	0,02
Manganèse	0,25	0,15	0,12	$\leqslant 0,5$
Tantale	$\ll 0,01$	$\ll 0,01$	$\ll 0,01$	$\ll 0,01$
Zirconium	$<0,2$	$<0,2$	$<0,2$	1.
Hafnium	$<0,01$	$<0,01$	$<0,01$	$<0,01$
Thorium (Pa)	$\ll 0,1$	—	—	$<0,002$
Chrome	$<0,1$	$<0,1$	$<0,1$	$<0,1$
Scandium	0,4–0,5	0,4–0,5	0,4–0,5	$\ll 0,01$
Yttrium	0,02–0,04	$\ll 0,001$	$\ll 0,001$	$\ll 0,001$
Lutecium	0,002–0,004	$\ll 0,0001$	$\ll 0,000.1$	$\ll 0,000.1$
Holmium	0,005–0,010	$\ll 0,0001$	$\ll 0,000.1$	$\ll 0,000.1$
Gadolinium	0,02–0,04	$\ll 0,01$	$\ll 0,01$	$\ll 0,01$
Terbium	0,003–0,006	$\ll 0,001$	$\ll 0,001$	$\ll 0,001$
Samarium	0,005–0,010	$\ll 0,00.1$	$\ll 0,000.1$	$\ll 0,000.1$
Néodyme	0,10–0,20	$\ll 0,01$	$\ll 0,01$	$\ll 0,01$
Praseodyme	0,05–0,10	$\ll 0,001$	$\ll 0,001$	$\ll 0,001$
Cerium	0,30–0,60	$\ll 0,01$	$\ll 0,01$	$\ll 0,01$
Lanthane	$\sim 0,01$	$\ll 0,001$	$\ll 0,001$	$\ll 0,001$
Nickel	2,5	$\leqslant 1.$	$\leqslant 0,5$	0,5
Cadmium	3,5	0,025–0,070	$\leqslant 0,002$	$\ll 0,01$
Cobalt	$\leqslant 0,010$	$\leqslant 0,010$	$\leqslant 0,01$	0,25
Zinc	17–20	1.	$\leqslant 0,05$	$<0,01$
Calcium	4–5	$\leqslant 0,5$	$\leqslant 0,5$	$<0,5$
Strontium	$\ll 1$	$\leqslant 0,5$	$\leqslant 0,5$	$<0,5$
Sodium	2	$\leqslant 0,2$	$\leqslant 0,2$	$<0,01$
Potassium	$<0,01$	$<0,01$	$<0,01$	$<0,01$
Rubidium	$<0,01$	$<0,01$	$<0,01$	$<0,01$
Caesium	$<0,01$	$<0,01$	$<0,01$	$<0,01$
Dosages sur prises séparées				
Baryum	6 ± 1	$0,03 \pm 0,005$	$0,03 \pm 0,005$	—
Chlore	$\ll 0,01$	$\ll 0,01$	$\ll 0,01$	$\ll 0,01$
Brome	$\ll 0,01$	$\ll 0,01$	$\ll 0,01$	$\ll 0,01$
Iode	$\ll 0,001$	$\ll 0,001$	$\ll 0,001$	$\ll 0,001$
Phosphore	3	—	0,04	$\leqslant 0,02$
Soufre	15	—	$1 \pm 0,5$	$\leqslant 0,5$
Carbone	1–2*	1–2*	—	10–25†

* Dosage par irradiation dans les Deutons. † Dosage par oxydation de C en CO_2.

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Ce qui caractérise cette méthode, ce sont les rendements en général très élevés des séparations chimiques effectuées. Dans le cas des métaux de haute pureté elle s'applique très aisément et permet de s'assurer très rapidement de la pureté globale d'un produit en ce qui concerne environ quarante à cinquante éléments. Dans le cas du fer purifié par " zone fondue ", elle permet de mettre en évidence, dans l'exemple donné, une pollution en cuivre et molybdène provoquée par une nacelle insuffisamment pure. Dans le cas de l'aluminium purifié par " zone fondue ", elle montre la très grande pureté du métal obtenu et révèle que les impuretés principales en ce qui concerne les éléments dosés sont alors le scandium (qui se trouvait à une faible concentration relative dans l'aluminium industriel) et le manganèse.

Evidemment, tous les éléments qui peuvent être dosés avec sensibilité par irradiation dans les neutrons, ne sont pas susceptibles d'être isolés dans une telle systématique. Aussi, un certain nombre d'éléments sont dosés sur des prises d'essais séparées: baryum, chlore, soufre, phosphore, silicium.

CONCLUSIONS

Sur une prise de l'ordre de 1 g, après irradiation de une semaine dans un flux de l'ordre de 10^{12} neutrons cm^{-2} sec^{-1} nous pouvons, dans des métaux purs, doser environ une quarantaine d'éléments avec une sensibilité comprise entre 0,1 et 0,0001 parties/million (*Tableau 3*).

Tableau 3

$2{,}5 \times 10^{11}$ neutrons $cm^{-2}sec^{-1} \longrightarrow 10^{-1}$ µg
5×10^{12} " $\longrightarrow 5 \times 10^{-2}$ µg
1×10^{14} " $\longrightarrow 2{,}5 \times 10^{-4}$ µg

Na											Al		P		Cl	
K		Sc		V	Cr	Mn		Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr		Mo		Ru		Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl				

Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	U												

Tableau 3. Les sensibilités susceptibles d'être obtenues dans les dosages par radioactivation des éléments indiqués pour des flux de neutrons indiqués (d'après W. W. Meinke, *Science*, **121**, 177 (1955))

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DETERMINATION OF TRACE ELEMENT DIFFUSION IN QUARTZ AND IN GERMANIUM

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Les problèmes de répartition des constituants mineurs dans le quartz et le germanium très pur ont été étudiés au moyen d'analyse par activation.

Two problems have been studied. One concerns the mercury distribution in quartz mercury vapour tubes. The other concerns the arsenic and phosphorus distribution in electronically pure germanium samples.

MERCURY DISTRIBUTION IN QUARTZ TUBES

By neutron irradiation of mercury the radioisotopes ^{197}Hg ($t_{\frac{1}{2}} = 65$ h), ^{203}Hg ($t_{\frac{1}{2}} = 47$ d) and ^{205}Hg ($t_{\frac{1}{2}} = 5{\cdot}5$ min) are obtained. The short-lived ^{205}Hg cannot be used for a study of the radial distribution as it necessitates a chemical attack and separation procedure. In our problem a longer activation time is needed in order to determine at least 10 parts/million of mercury in 10 mg amounts of silica matrix. We can calculate that a seven-day irradiation at the neutron flux available of 10^{12} neutrons cm^{-2} sec^{-1} provides the initial activities represented in *Table 1*. The induced activities of interfering elements are also given.

As can be seen from *Table 1*, the activities of ^{197}Hg and ^{203}Hg produced are sufficient for the determination of 0·1 μg of mercury. The interferences due to ^{64}Cu, ^{42}K, ^{24}Na, ^{187}W and ^{76}As are slight after 8 days. Interferences, however, due to ^{124}Sb, ^{110m}Ag, ^{182}Ta and ^{65}Zn, increase as a function of time, which makes chemical separation necessary.

When mercury is precipitated as the sulphide in 1N hydrofluoric acid after addition of mercury carrier, good decontamination can be obtained from the isotopes ^{65}Zn, ^{187}W, ^{24}Na, ^{42}K and ^{182}Ta. On the other hand co-precipitation of antimony, arsenic, copper and silver can occur.

The activity measurement of the isolated mercury can be made in two ways:

Beta measurement is less interesting because the maximum beta energy of ^{203}Hg only amounts to 208 keV and the electron capture (E.C.) of ^{197}Hg can only be measured indirectly, and with low efficiency, by the K_x radiation.

Gamma measurement can be carried out on the 279 keV photo-peak of ^{203}Hg. The sensitivity, however, is considerably better when the 77 keV transition of ^{197}Hg is measured. Using a gamma spectrometer, impurities which occur occasionally can also be detected, and the results corrected for these.

Experimental

Two quartz samples and a mercury standard are irradiated simultaneously for 7 days at a neutron flux of 5×10^{11} neutrons cm^{-2} sec^{-1}.

Table 1. Interference of trace elements: 7-day irradiation; flux = 10^{12} neutrons cm^{-2} sec^{-1}

Element	*Occurrence* (parts/million)	*Isotope formed*	$t_{\frac{1}{2}}$	$E\beta$ max (MeV)	E_γ (MeV)	*Activity* at end of irradiation*
As	10^{-2}–1	^{76}As	26·4 h	β^-2·97 2·41 1·76	0·555 1·210 2·06	$3·38 \times 10^4$
Zn	0·4	^{65}Zn	245 d	β^+0·324 E.C.	1·14 0·82 0·511	$4·9 \times 10$
W	0·5	^{187}W	24·0 h	β^-0·63 1·33	0·072 0·686	$3·2 \times 10^4$
Na	0·1	^{24}Na	15 h	β^-1·39	1·368 2·758	$1·4 \times 10^4$
K	1	^{42}K	12·5 h	β^-3·55 1·99	1·53 0·309	$7·3 \times 10^4$
Ta	10	^{182}Ta	115 d	β^-0·514 0·44 0·36	0·06 1·2	$3·2 \times 10^3$
Cu	0·2	^{64}Cu	12·8 h	E.C. β^+0·19 β^-0·39	0·511 1·34 (0·5%)	$2·8 \times 10^4$
Sb	1	^{122}Sb ^{124}Sb	28 h 60 d	β^+/K.C. β^-2·31	0·56–1·2 0·6–2·1	$3·7 \times 10^3$ $4·25 \times 10^3$
Ag	1	^{110m}Ag	253 d	—	0·116 1·5	$1·7 \times 10^3$
Hg	10–100	^{203}Hg ^{197}Hg	47 d 65 h	β^-0·208 E.C.	0·279 0·077	$2·7 \times 10^3$ $1·13 \times 10^4$

* Disintegrations per second per microgram of element.

The quartz tubes with unknown mercury content are coated on the outside with paraffin, so that only the inside can be dissolved away.

The samples are successively weighed, treated with 38 per cent hydrofluoric acid containing one drop of concentrated nitric acid and washed twice with distilled water. This series of operations is repeated several times.

The hydrofluoric acid and washing solutions are combined in polythene centrifuge tubes. To each of these mercury-containing solutions 2 ml of mercuric nitrate solution (0·9 mg Hg/ml) is added as a mercury carrier. The solutions are mixed homogeneously and further acidified with nitric acid ($d = 1·40$) in order to minimize co-precipitation of copper, antimony and arsenic sulphides.

The mercury is precipitated as sulphide, the supernatant solution is decanted after centrifugation. The mercuric sulphide residue is washed twice with a dilute solution of hydrofluoric (1N) and nitric (0·1N) acids and once with distilled water. Filtration is finally done on SS 589[3] filter paper or on porcelain filtering discs. The standard is treated in the same way.

Activity measurements—The low gamma and beta energy of the mercury isotopes formed permit easy purity control. Measurements have been done by means of the multichannel RCL 256 gamma-ray spectrometer of

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the Physics Department. As a result only ^{122}Sb seemed to be a source of interference, particularly when measuring gamma radiation above 200 keV. The disintegration ratio of ^{122}Sb and ^{203}Hg has been derived from the surface ratio of the respective photo-peaks and amounts to 19 per cent in the worst cases—two days after the end of irradiation.

From this statement it seems that further purification of the isolated mercuric sulphide is necessary. However, in gamma-ray measurements between the limits of 60 and 85 keV interference by ^{122}Sb is negligible. Under these measuring conditions no further purification is needed.

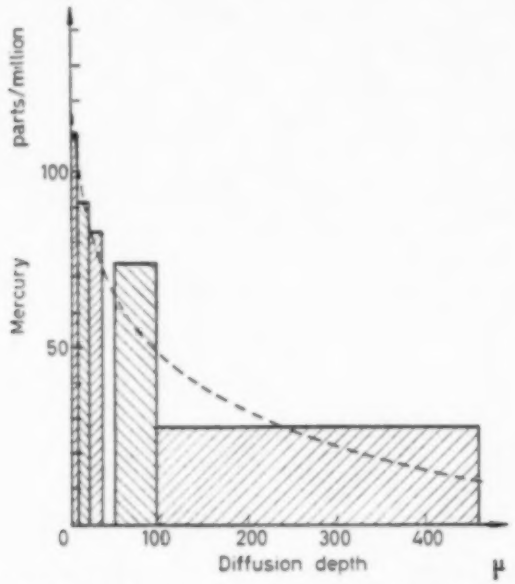

Figure 1. Diffusion of mercury in quartz tubes (N. V. Philips Monster 5)

Results

The radial distribution of mercury as found by activation analysis is represented in *Figure 1*. The mercury content decreases noticeably with increasing depth. The results allow the determination of the total energy from the diffusion depth of the activated mercury atoms to be made.

PHOSPHORUS AND ARSENIC DISTRIBUTION IN GERMANIUM SAMPLES

The determination of arsenic impurities and other trace elements in germanium by means of activation analysis has been worked out by several authors. Smales and Pate[1] were the first to determine submicrogram amounts of arsenic in a germanium matrix. Their method involves a chemical separation procedure based on the distillation of germanium as germanium tetrachloride, followed by distillation of arsenic as arsenic tribromide, in a second fraction. In 1956 Morrison and Cosgrove[2] and

J. V. Jakovlev[3] published their results on the activation analysis of impurities in germanium obtained by using γ-spectrometry as a tool to simplify or to eliminate chemical procedures.

No results have been found in the literature about the determination of phosphorus in high-purity germanium.

For the determination of phosphorus and arsenic distribution gradual dissolution of the germanium sample is necessary, followed by the analysis of the respective fractions. The distillation procedure according to Smales and Pate is rather tedious for the simultaneous analysis of six to eight fractions. Solvent extraction procedures[4, 5] also have been described which provide an enrichment factor for ^{76}As of between 10^4 and 10^5. However, they do not permit simultaneous analysis of the different fractions by one operator. The most promising enrichment method seems to be an ion-exchange procedure. Indeed, interesting work has been done in that field: Irvine and co-workers[6] prepared carrier-free ^{74}As by eluting the As^{3+} from Dowex I by means of 0·5–2·5N hydrofluoric acid solution. Further Kraus and co-workers[7, 8] published distribution data on germanium and arsenic in hydrochloric and hydrochloric–hydrofluoric acid media. As the chief contaminant apart from ^{77}As seems to be ^{32}P, we required conditions under which arsenic is selectively eluted. Batch experiments in ammonium fluoride–hydrofluoric acid media indicated great differences

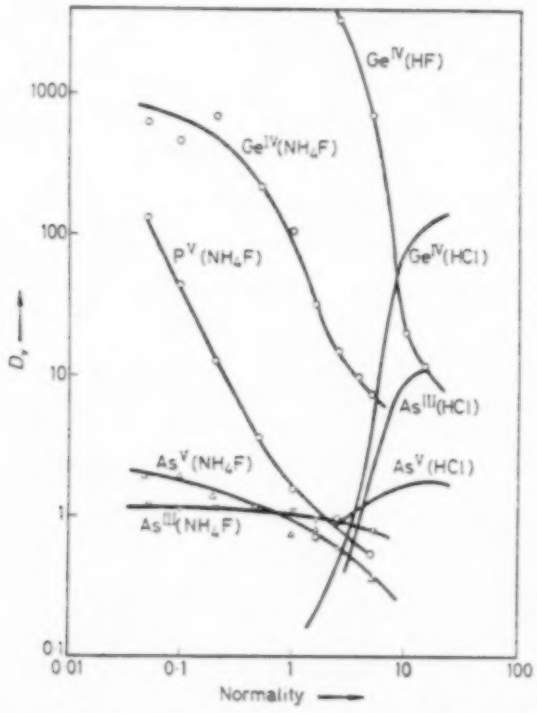

Figure 2. Distribution coefficients (D_E values) as functions of HF, HCl and NH_4F concentrations

in the distribution coefficients (D_v values) of Ge^{IV}, P^V and As^V, as is shown in *Figure 2*. However, column experiments did not agree with the values under batch conditions. Eventually elution in hydrofluoric acid medium was applied, followed by a chemical separation of arsenic and phosphorus.

Experimental

For analysis of the radial distribution of arsenic and phosphorus, a cylindrical germanium sample weighing about 4 g is irradiated for 24 h in a neutron flux of 10^{12} neutrons cm^{-2} sec^{-1}. Standard samples containing ammonium dihydrogen phosphate, ammonium sulphate and arsenious oxide and a small piece of germanium are added.

One hour after irradiation the samples are dissolved gradually in a mixture of 3 ml of concentrated hydrofluoric acid and 0·5 ml of nitric acid ($d = 1{\cdot}40$). To the fractions obtained 5 mg of arsenic and 5 mg of phosphorus carrier are added, after which the solutions are diluted with distilled water until 0·5N with respect to hydrofluoric acid.

The solutions are poured onto Dowex I (8 columns 12 cm high, 1·2 cm diameter). As^V and P^V are then eluted with 100 ml of 0·5N hydrofluoric acid. To the eluate are added immediately 0·5 g of boron trioxide and 3 drops of a 10 per cent solution of potassium iodide, after which arsenic trisulphide is precipitated by means of hydrogen sulphide. The solution is kept for 2 h at 80°C, and saturated again with hydrogen sulphide. The precipitate is filtered off on SS 589³ filter paper and washed with 20 ml of 0·5N hydrofluoric acid.

The filtrate containing ^{32}P is further acidified by means of nitric acid ($d = 1{\cdot}40$) until a 2N nitric acid solution is obtained. Since fluoride ions are masked by the boric oxide, phosphorus can be precipitated as ammonium phosphomolybdate. The precipitate is filtered off on SS 589³ filter.

Measurements of ^{76}As in the ^{76}As–^{77}As mixture are made by means of an anthracene detector beta spectrometer. The ^{32}P is measured by means of a Geiger–Müller detector. Purity is checked by gamma spectrometry and decay control.

Discussion of results

The results obtained indicate the presence of 0·10–0·15 parts/million of arsenic throughout the germanium sample. Phosphorus content, on the other hand, is lower than 10 parts/million, and seems to be slightly enriched on the outer side of the sample.

The formation of ^{32}P from $^{32}S(n,p)^{32}P$ cannot be regarded as an important source of error under the irradiation conditions. This has been proved by the specific activities of ^{32}P formed by (n,γ) and (n,p) reactions. The absence of chlorine has also been demonstrated.

Difficulties arise from the necessity of dissolving the germanium sample gradually. In order to avoid errors due to neutron shadow, the germanium sample is weighed after each dissolution process. Two days after irradiation of the germanium samples the ^{77}As is milked off again. The specific activity due to ^{77}As is compared for each fraction and with that of a small germanium monitor sample.

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DISCUSSION

K. LJUNGGREN (*Sweden*): Metallurgy seems to be a field in which it is very appropriate to use an inactive tracer which is then determined by radioactivation analysis. In some recent work carried out in Sweden gold has been used as a tracer for determining the refractory wear of an electric steel furnace. Suitable amounts of gold were added to the refractory bricks in the bottom of the furnace. In a series of runs samples were taken of consecutive steel melts and analysed for gold by radioactivation. A rapid chemical separation was used because of an interfering chromium activity in the stainless steel. Concentrations of gold down to 0·01 parts/million were easily detected. We have also used lanthanum and dysprosium for the labelling of slag, both in order to determine the total amount of slag, and also to investigate the origin of non-metallic inclusions.

A METHOD FOR THE DETECTION OF MERCURY BY RADIOACTIVATION ANALYSIS

K. LJUNGGREN* and T. WESTERMARK

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Une methode d'analyse par radioactivation est presentée, laquelle a été utilisée pour la determination du mercure dans les échantillons biologiques, l'aluminium, la cellulose et les grains traités par des composés de phenylacetate de mercure. Une des diffucultés rencontrees dans cette experience est due à l'évaporation du mercure dans le réacteur. Cette dernière a été vaincue en scellant les échantillons dans des ampoules de quartz standardisées.

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A method which has been developed by Westermark and Sjöstrand[1,2] in Sweden, has been used for the determination of mercury in biological samples, aluminium, cellulose and grains treated with mercury-phenylacetate compounds. In the last two cases the method has competition from the highly developed flame method, but will possibly be of value for confirmations. In the first two cases the activation analysis method is valuable.

In activation analysis of mercury by means of neutron irradiation one has to choose between measurements on ^{203}Hg and ^{197}Hg. The former has a half-life of 48 days and the latter of 25 and 65 h, respectively, in two isomeric states. The use of ^{197}Hg can be shown to give a sensitivity 50 times that for ^{203}Hg for a one-week irradiation. The latter alternative should be used only if work close to a reactor is not possible.

^{197}Hg is a very favourable case for non-destructive spectrometric determination. The 65-hour isomer which has a much higher cross-section than the 25-hour ^{197m}Hg decays by *K*-capture, followed by a 77 keV gamma emission, to ^{197}Au. The method has been based on the measurement of the 77 keV line which is readily detected in ordinary sodium iodide crystals, which is a great advantage. However, optimal conditions may arise with the use of wafer crystals which we have heard much about earlier in this symposium.

A unique difficulty which has been encountered in the work with mercury, is evaporation due to the elevated temperature in the reactor which in the actual irradiation positions is 40°–60°C. The temperature of the sample may be still higher owing to radiation absorption. Even when the mercury has been treated with hydrogen sulphide, it does not remain quantitatively in the cellulose at higher temperatures.

A quartz ampoule technique has therefore been devised. The samples and the standards, which consist of mercuric chloride treated with hydrogen sulphide, are enclosed in quartz ampoules which are sealed while the sample is protected by cooling. The spectrometry is carried out without opening the quartz containers. The induced activity in the quartz is therefore of importance. It has been found possible to measure the mercury line without interference if an ageing period of two days is used. After this

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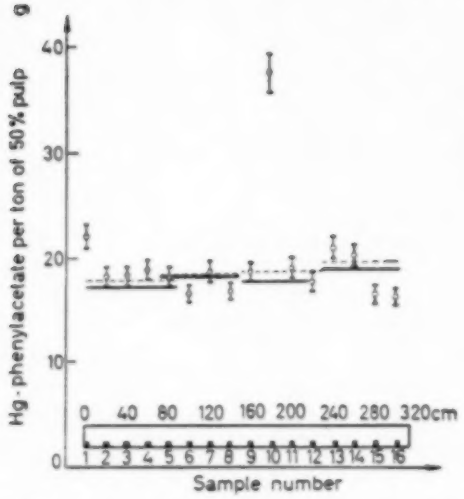

Figure 1. Amount of mercury-phenylacetate in samples taken across pulp bed determined by activation analysis (°) and chemically (- - - and ——)

period silicon and sodium activity from the quartz, and sodium and often copper and manganese from the sample, have decayed sufficiently.

By this method mercury has been determined in mechanical pulp (*Figure 1*); individual grains; brain and liver tissue from (living) rabbits exposed to mercury-containing atmospheres; human faeces (exposure of industrial workers to mercury); aluminium in corroded form; samples of the remains of King Erik XIV who died in 1577.

The sensitivity limit of the method in its present form is 0·03 μg with a precision of 5–15 per cent after irradiation for 3 days at 1–2 $\times$ 10^{12} neutrons $cm^{-2}\,sec^{-1}$. The method has been checked by analysis of a series of prepared samples (*Figure 2*).

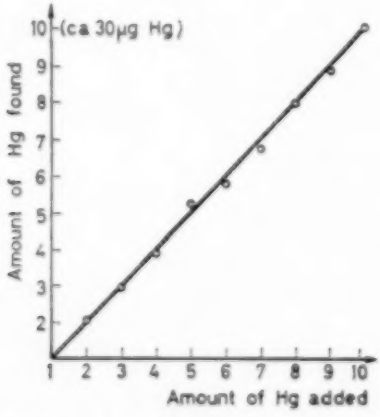

Figure 2. Accuracy test for activation analysis method
Relative units: 1 unit $\simeq$ 3 μg.

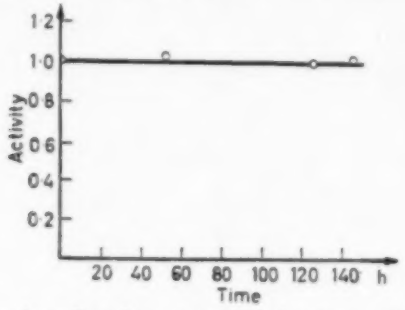

Figure 3. Activity of peak attributed to mercury relative to mercury standard against time after irradiation

Considerable experience has been gained with the method in that several hundred samples have been analysed. Difficulties due to ^{32}P bremsstrahlung were encountered in attempts to analyse bone from humans. This may possibly be overcome by the subtraction method as it has been applied in similar cases by Dr Leddicotte.

Improvements in the method may be accomplished by the use of proportional counter spectrometry since the γ-line is converted to an appreciable degree. In this case the ampoules have to be opened before the measurement. In the near future the high flux of the material testing reactor R2 will become available, which will greatly enhance the possibilities of this and other activation analysis work in Sweden.

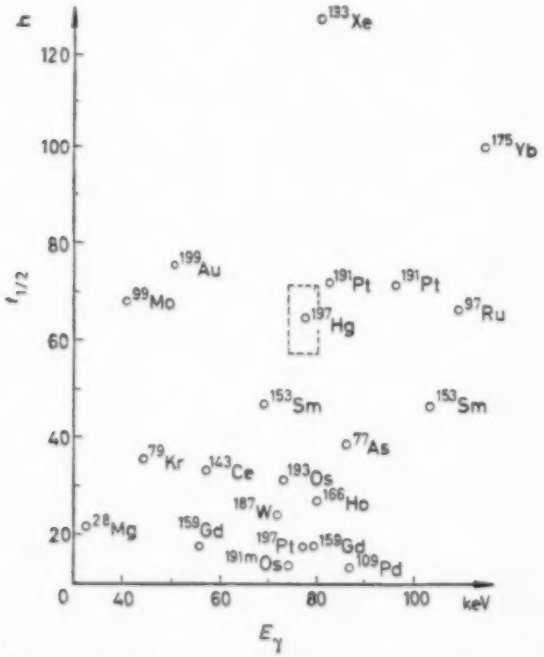

Figure 4. Part of $t_{\frac{1}{2}}$–$E\gamma$ chart for nuclides surrounding ^{197}Hg

In connection with the determination of mercury in the royal remains of Erik XIV the question arose of a definite positive identification of elements present in a sample. One method of systematizing such work has been given by Westermark[3]. From a series of spectra the energy of the photo-peak in question is determined together with the uncertainty in the energy. The decay of the photo-peak is followed, and compared with that of the irradiated standard. If the measured peak really belongs to the same element as the standard this ratio will be constant (*Figure 3*).

From a series of such decay measurements the uncertainty in the half-life can be obtained. Now the half-life and energy values are entered together with the determined uncertainties in a diagram which represents all nuclides produced by (n,γ) reactions. As is seen in *Figure 4*, the isotopes are presented as points in a diagram where energy is given as the abscissa and the half-life as the ordinate. As long as the uncertainty rectangle only contains one nuclide, and is far from others, the identification is positive.

In conclusion, the determination of cobalt in steel by means of the short-lived activity ^{60m}Co, which was reported at the last Geneva Conference, has been continued on iron ores where the same method is applicable. It has been interesting to hear that Dr Meinke has also been working on this cobalt isotope. The results lie between 30 and 100 parts/million in general, but one ore has been found which contains as little as 2 parts/million. This is of very great importance indeed in the manufacture of material used in the construction of reactors where the induced cobalt activity is a great disadvantage.

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DISCUSSION

A. H. W. Aten (*Netherlands*): Has the graph of γ-ray energies against half-life been published?

K. Ljunggren (*Sweden*): The identification method will be published in the *Journal of Applied Radiation and Isotopes*.

G. W. Reed (*U.S.A.*): We can confirm Dr Ljunggren's experience with the instability of mercury in monitors irradiated in a reactor. We finally relied on the addition of sulphide ions to monitors spiked with mercury. We could not, however, measure the monitor mercury without doing chemistry. The sealed quartz vials are chilled with dry ice, cracked open and placed immediately in hydrochloric acid solution containing mercury carrier. Since Hg and Hg^{+} exchange very rapidly, no trouble with tracer loss or radiochemical equilibration should exist.

While speaking of equilibration I should like to point out the following. In preparing samples for analysis after irradiation, whether by acid dis-

solution or fusion, the carrier should always be present at the time the sample is dissolved. In this way the carrier is always present in high concentration, which avoids loss of the desired tracer by absorption on walls or possibly even by volatilization.

A. H. W. ATEN (*Netherlands*): In our Institute we do not have a whole department for activation analysis, so you must not expect any complete descriptions of technical procedures from me. I can only give you some rather general remarks concerning the advantages and drawbacks of fast neutron activation.

A cyclotron produces quite a lot of neutrons, but they are formed with quite high energies and to make them thermal we have to use a lot of paraffin or other moderator, which means that the thermal flux obtainable is rather low.

It is therefore interesting to see what one can do with fast neutrons. Samples for fast neutron irradiation can be placed very near the target, and then the flux is several orders of magnitude higher.

I wish to make it clear that a cyclotron is by no means the ideal instrument for fast neutron activation analysis. With a cyclotron:

(1) It is almost impossible to irradiate several samples at the same time in identical positions.

(2) It is not easy to put several samples into exactly the same spot for a series of successive irradiations.

(3) It is often difficult to keep the beam current constant.

(4) The energy of the neutrons does not have a definite value, but varies over a large range. (The best neutron production is obtained by bombarding beryllium with deuterons.)

I have no experience with the (D + T) reaction, but I did work with an accelerator giving (D + Li) neutrons during the war. I have the impression that, in general, accelerator tubes will be more satisfactory for fast neutron activation analysis, unless one wishes to use a high flux. For activation analysis work with a machine factors come into play which are of no importance to people who use a reactor.

The most important point is that irradiation time with an accelerator is very expensive, so one tends to choose a nuclide with a short half-life, so as to reach or approach saturation as quickly as possible.

Also the individual cross-sections of the different nuclides do not vary nearly as much for fast neutrons as they do for slow neutrons, although the differences are still important enough to influence the choice of our reaction. Then one has to keep in mind that with fast neutrons quite a number of different types of reactions may occur with cross-sections that are not too different: (n,2n), (n,p), (n,α) and—at least with a cyclotron—also (n,γ).

Fast neutron activation is of particular interest for those elements among the rare earths with which slow neutron activation is not very successful, that is, for the lightest elements, lanthanum, cerium, praseodymium and neodymium.

The target material should be in the form of the oxide, which means that ^{15}O will be produced by the $^{16}O(n,2n)^{15}O$ reaction. ^{15}O is a positron emitter with a half-life of 2 min. A correction is easily made as it is recognized by its half-life, and its intensity can be measured by a separate

irradiation of a compound which gives essentially pure ^{15}O activity. For this purpose we irradiate lithium carbonate. Some ^{11}C is produced by the $^{12}C(n,2n)^{11}C$ reaction, but the amount is negligible if the irradiation time is comparable to the half-life of the oxygen.

To get the highest accuracy one would of course have to use an internal standard, but for approximate determinations such as for checking the purity of materials, one may integrate the beam current over the irradiation period and obtain quite reasonable results. If the beam current is not constant the irradiation time should be comparable to the half-life of the radioisotope produced.

Irradiation of praseodymium with fast neutrons produces an appreciable quantity of ^{140}Pr by the $^{141}Pr(n,2n)^{140}Pr$ reaction. This praseodymium isotope is a positron emitter and has a half-life of 3·4 min. A 200 mg sample

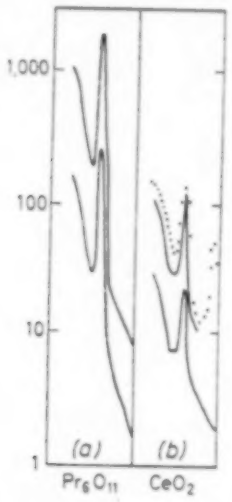

Figure 5. Spectra of irradiated praseodymium oxide (*a*) and cerium oxide (*b*)

of praseodymium oxide irradiated for 4 min in the Amsterdam cyclotron, and measured 3 min and 13 min after irradiation, gave the spectra shown in *Figure 5(a)*. It can be seen that in ten minutes the activity has decayed by a factor slightly less than ten, which agrees with a half-life of 3·4 min. The amount of ^{15}O produced is negligible, amounting to less than 1 per cent of the positron activity of praseodymium. However, this would not be the case if the praseodymium were an impurity present in small concentration in another rare earth oxide.

This reaction may be used for the detection of praseodymium in the oxides of other elements. *Figure 5(b)* shows the spectra obtained after irradiation of a sample of cerium oxide of unknown purity. The two spectra were measured 3 min and 13 min after the end of the irradiation. The latter spectrum shows the presence of the ^{140}Pr quite clearly. The spectrum obtained 3 min after the end of the irradiation is shown as the

dotted line in *Figure 5(b)*. To the right of the ^{140}Pr annihilation peak there is interference from a 0·74 MeV gamma line due to ^{139}Ce produced by the $^{140}Ce(n,2n)^{139}Ce$ reaction. Since the ^{139}Ce has a half-life of about 1 min this interference does not appear in the spectrum measured 13 min after the end of the irradiation. The spectrum obtained 3 min after irradiation shown by the full line in *Figure 5(b)* has been corrected by subtracting the spectrum obtained from an irradiated sample of very pure cerium oxide. The praseodymium content from both the three- and thirteen-minute spectra works out at about 6 per cent. This sample was of course a very crude cerium oxide and it would be quite possible to detect a much smaller amount of praseodymium.

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DETERMINATION OF TANTALUM IN HIGH-TANTALUM FERRO-ALLOYS

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Une methode est décrite pour la détermination rapide de forte concentration de tantale dans les alliages de fer utilisant l'activation neutronique, suivit par la mesure du rayon-gamma choisi. L'échantillon est irradié en solution pour éviter les erreurs de blindage contre les neutrons.

The determination of tantalum in ferro-alloys containing niobium is quite difficult, particularly on a routine basis. Since tantalum has a large slow neutron capture cross-section, and the radio-tantalum (^{182}Ta) produced on irradiation emits high-energy gamma-rays (1·12, 1·22 MeV), it should be an ideal element for non-destructive analysis by neutron activation and direct gamma-ray spectrometry.

The large slow neutron capture cross-section (22 barns) does, however, introduce neutron self-shielding errors in both samples and standards, and it was expected that some sort of " solid dilution " technique[1] using powdered graphite or sucrose as diluent would be necessary.

SELF-SHIELDING EFFECTS

Two samples were obtained for analysis and were originally supposed to contain about 5 per cent and about 20 per cent of tantalum. To assess the self-shielding effects, the samples (in the form of turnings) were irradiated as received, together with tantalum pentoxide standards. The induced activity at about 1·2 MeV was measured on a gamma spectrometer, the resolution of which was reduced so that the high energy gammas of tantalum-182 combined into a single flat-topped peak. As was expected, high results were obtained due to self-shielding in the tantalum standard. The results for the 5 per cent sample were, however, much higher, relatively, than those for the 20 per cent sample, thus indicating that there was also some self-shielding in the 20 per cent sample.

Attempts were made to eliminate these effects by mixing the samples and standards with powdered graphite or sucrose (previously shown to contain a negligible amount of tantalum), but at best this only partially reduced the self-shielding effects. This was attributed to the comparatively large particle size of the sample and standard; although the particles were dispersed in the graphite, self-shielding still occurred within the individual particles.

This was confirmed by preparing a series of tantalum solutions of increasing concentration (up to 30 mg/ml) and irradiating equal volumes of each. A plot of induced activity against weight of tantalum then gave a typical self-shielding curve with an observed reduction in activity of

30 per cent at 30 mg/ml of tantalum. It is interesting to note that the formula of Keyes[2] indicates that the self-shielding should be negligible at this dilution. From the graph it was possible to calculate the specific activity which would have been obtained in the absence of self-shielding, and this was shown to be greater than that obtained from a single grain of tantalum pentoxide. When a solution of tantalum, of such dilution that the self-shielding error was less than 1 per cent was used as standard, low results were obtained. The results for the 20 per cent alloy were much less, comparatively, than those for the 5 per cent alloy, thus confirming that self-shielding effects were still operating even in these samples.

Two methods of approach were now available: to prepare standards of the same tantalum content as the samples (either in solution or, preferably, in alloy form); or to dissolve both standards and samples and to dilute the solutions to the same concentration. The latter procedure was in fact chosen. If the samples and standards are both diluted to a concentration less than that giving 1 per cent self-shielding error, the two concentrations need not be matched exactly; but if a preliminary analysis is made to enable the concentrations to be matched fairly closely, much higher concentrations and therefore shorter irradiation times can be used.

The alloy samples and the tantalum metal standard were dissolved in hydrofluoric acid, containing the minimum of nitric acid, in platinum dishes. The solutions were diluted by weight in polythene bottles. A thulium-170 source was used as a static eliminator to facilitate these weighings. The first set of solutions for irradiation were heat-sealed in polythene tubes (pill-packs) but variable results ($\pm$ 10–15 per cent) were obtained. This effect was attributed to incomplete sealing, although usually this was satisfactory, and in all subsequent irradiations silica ampoules were used, giving a reproducibility better than 5 per cent. Since high concentrations of tantalum were involved, reagent blanks were not important, but it was established that the acids used contained negligible amounts of tantalum.

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METHOD

Prepare matched solutions of standard and sample in the range of 5–10 mg/ml of tantalum. If solutions cannot be matched, dilute to less than 2 mg/ml of tantalum for less than 1 per cent self-shielding. Irradiate weighed 0·2 ml portions of these solutions in a neutron flux of 10^{12} neutrons cm^{-2} sec^{-1} for 30 min, or proportionately longer for the more dilute solutions or lower fluxes. Allow 24 h for short-lived activity to decay, then determine the tantalum activity on a gamma-ray spectrometer using a scaler connected into a fairly wide channel (about 5 V). If a spectrometer is not available, use a normal gamma-ray counter biased so that it just counts the high energy tantalum activity. Compare the activities of standards and samples, and calculate the results in the usual way.

Results

	Ta *present*	Ta *found*
Sample 1	13·18%	13·1 $\pm$ 0·3%
Sample 2	19·4%	20·0 $\pm$ 1·0%
Sample 3	5·2%	5·7 $\pm$ 0·2%

All errors represent *maximum* experimental variations.

Sample 1 is a standard alloy with an agreed average value.

Sample 2. The value 19·4 per cent for the tantalum content is the mean of 18·4 per cent (Swedish referee), 18·6 per cent (British referee) and 21·3 per cent (industrial analysis).

Sample 3. The value 5·2 per cent is from an industrial analysis, and no explanation has so far been found for the discrepancies in the results for this sample.

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INTERMETALLIC DIFFUSION IN GOLD-LEAD SYSTEMS

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Quelques resultats préliminaires sur la diffusion de l'or dans le plomb, obtenus par l'utilisation des traces radioactives, sont presentés.

One of the most typical applications of radioactive tracers in basic solid state physics and metallurgy is in the study of self-diffusion and inter-diffusion phenomena in solids and liquids.

Some results concerning the diffusion of gold in lead are briefly reported here. The general procedure involved is well known: a thin layer of a suitable radioactive isotope is plated onto the specimen to be investigated and, after a sufficiently long annealing interval, at high temperature, the distribution of activity within the specimen is studied by a sectioning and counting technique. It is found that the activity $A(x)$ at a distance x from the surface is given by

$$A(x) = \frac{c}{t^{\frac{1}{2}}} \exp\left(-\frac{x^2}{4Dt}\right)$$

where D is the diffusion coefficient at the temperature T, and c is a constant.

D depends upon temperature according to the law

$$D = \mathrm{D}_0 \exp\left(-\frac{Q}{kT}\right)$$

Q represents the activation energy for diffusion in the case in question. Previous research on the gold–lead system was done in 1933–1935, mainly by Seith, who used chemical methods in tracing gold atoms in the lead matrix. Rather large amounts of gold were needed. As D is expected to depend upon the mutual concentrations of the two elements it was thought convenient to repeat such measurements, using very small concentrations of radioactive gold.

PRESENT MEASUREMENTS

The use of radioactive tracers provides an extremely sensitive method of identifying very small amounts of gold within lead, and makes it possible to measure the diffusion coefficient of gold in pure lead. In a first run of measurements very pure lead (99·998 per cent) was used in the shape of cylindrical polycrystals 15 mm long and 1 cm in diameter, and of foils $\frac{1}{10}$ mm thick, 1 cm wide and 4 cm long.

Annealing was done in a furnace where the temperature was uniform and stabilized within $\pm 0{\cdot}4$°C, between 180°C and 300°C. Owing to the short half-life of ^{198}Au produced in the reaction

$$^{197}\mathrm{Au}(\mathrm{n},\gamma)^{198}\mathrm{Au} \longrightarrow \beta^- + {}^{198}\mathrm{Hg}(t_{\frac{1}{2}} = 2{\cdot}7\ \mathrm{d})$$

a slightly unconventional experimental procedure was used. It was made possible by the small activation cross-section of lead and the short half-lives of the lead isotopes, and was as follows:

(1) Inactive gold was evaporated onto the specimen.
(2) Diffusion annealings were done at the different temperatures.
(3) Diffused samples were activated at Harwell.
(4) Specimens were sectioned (50 μ thick), and the distribution of gold was measured by counting the activity due to the 411 keV γ-rays from ^{198}Au.

The results suggested the following law

$$D = 2{\cdot}8 \times 10^{-3} \exp\left(-\frac{0{\cdot}39}{kT}\right) \mathrm{cm}^2\ \mathrm{sec}^{-1} \qquad (Q \text{ in eV})$$

Such results noticeably differ from those given by Seith:

$$D_0 = 2{\cdot}8 \times 10^{-3} \text{ instead of } 0{\cdot}4 \times 10^{-3}$$
$$Q = 0{\cdot}39 \text{ instead of } 0{\cdot}60$$

The disparity is not due to the effects of surface diffusion, as we found the same results with cylindrical probes and with thin foils. There are three further possible explanations:

(1) The irradiations after diffusion were performed at a low temperature (37°C), but it cannot be excluded that the temperature might have been somewhat higher so that some further diffusion might have taken place during irradiation.

(2) Diffusion at grain boundaries could have been considerable in the polycrystalline specimens. (Some of Seith's specimens were single crystals.)

(3) The fast neutron flux within the reactor might have had the effect of enhancing the diffusion process even at low temperatures. (This effect has been recently noted by Dienes and Damask in α-brass.)

Rough calculations were tried to test (1) and (3); it was concluded that their effect must have been rather small, and have tended to reduce the discrepancy. Further measurements were done by one of us (A.A.) with an entirely different procedure in order to compare diffusion coefficients in single crystals and in polycrystals, and to eliminate any possible spurious effects.

Single lead crystals were grown from high-purity lead as cylinders, 1 cm in diameter, 4 cm long. One of the ends was flattened by alternative sectioning and etching: this method was found to be effective in maintaining the single crystal structure of the specimens.

Carrier-free ^{195}Au($t_{\frac{1}{2}} \simeq 200$ d) was obtained from Philips Roxane after deuteron irradiation of platinum, and was electroplated in very thin films

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onto lead. After annealing, the specimens were sectioned (20 μ thick) and the activity due to kx-rays from lead (^{195}Au decays by electron capture to Pb) measured by means of a scintillation spectrometer.

The investigated range of temperatures was widened between the melting point of lead (327°C) and 120°C. The results are not yet complete. The results obtained so far suggest that

$$D_0 \simeq 6{\cdot}4 \times 10^{-3}\ \text{cm}^2\ \text{sec}^{-1}, \qquad Q \simeq 0{\cdot}45\ \text{eV}.$$

It can therefore be deduced that none of the three effects listed changes the measured diffusion rate to any marked extent. Corrections to the previous results would tend to make the two curves coincide, but it is too early to form a definite opinion on this point.

If the two series of results are assumed to be equivalent, the parameters of gold–lead diffusion turn out to be

$$D_0 \simeq 1{\cdot}2 \times 10^{-2}\ \text{cm}^2\ \text{sec}^{-1}, \qquad Q \simeq 0{\cdot}46\ \text{eV}$$

which must probably be considered as the upper limit. We consequently conclude that the activation energy for the diffusion of gold in lead is smaller than previous results seemed to indicate. It is nevertheless remarkable that such reasonably accurate results were obtained even before radioactive tracers were available.

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SECTION OF ANALYTICAL CHEMISTRY

COMMISSION ON MICROCHEMICAL TECHNIQUES*

RECOMMENDED TEST SUBSTANCES FOR THE MICRODETERMINATION OF CARBON AND HYDROGEN

A number of compounds are recommended for use as test substances for the microdetermination of carbon and hydrogen in organic substances. All of these substances, or a proper selection from the list, may be used to determine the universal applicability of a given method, either already described or one which might be developed in the future.

The compounds selected are stable over long periods of time and are non-hygroscopic (any exceptions to the latter generalization are noted). The substances are either commercially available in a sufficiently pure state to be used for tests based on the accuracy of present-day methods, or may be purified or prepared by conventional laboratory means to meet these standards.

The compounds selected include the following:

(1) those which have extreme values (high as well as low) for carbon and/or hydrogen contents;

(2) compounds representing a variety of structural types;

(3) compounds containing elements which may cause interferences in the carbon–hydrogen determination.

These recommendations may be changed or supplemented as the need arises.

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	Empirical formula	*Molecular weight*	C (%)	H (%)	O (%)	N (%)	Hal (%)	S (%)	Element (%)
C,H									
Anthracene	$C_{14}H_{10}$	178·234	94·34	5·66					
Cylohexane	C_6H_{12}	84·162	85·63	14·37					
Naphthalene	$C_{10}H_8$	128·174	93·71	6·29					
O (C,H)									
Benzoic acid	$C_7H_6O_2$	122·125	68·85	4·95	26·20				
Cholesterol	$C_{27}H_{46}O$	386·665	83·87	11·99	4·14				
d-Glucose (dextrose)	$C_6H_{12}O_6$	180·162	40·00	6·71	53·29				
Phthalic acid anhydride	$C_8H_4O_3$	148·120	64·87	2·72	32·41				
Stearic acid	$C_{18}H_{36}O_2$	284·486	76·00	12·76	11·25				
N (C,H,O)									
Acetanilide	C_8H_9ON	135·168	71·09	6·71	11·84	10·36			
Caffeine (1,3,7-trimethyl-xanthine anhydrous)	$C_8H_{10}O_2N_4$	194·200	49·48	5·19	16·48	28·85			
2,4-Dinitrophenylhydrazine	$C_6H_6O_4N_4$	198·146	36·37	3·05	32·30	28·28			
Diphenylamine	$C_{12}H_{11}N$	169·228	85·17	6·55		8·28			
Hexamethylenetetramine	$C_6H_{12}N_4$	140·194	51·40	8·63		39·97			
Picric acid	$C_6H_3O_7N_3$	229·114	31·45	1·32	48·88	18·34			
F (C,H,O,..)									
p-Fluorobenzoic acid	$C_7H_5O_2F$	140·117	60·00	3·60	22·84		F (%)		
Perfluorodicyclohexylethane	$C_{14}F_{26}$	662·154	25·39				13·56		
Trifluoroacetanilide	$C_8H_6ONF_3$	189·144	50·80	3·20	8·46	7·41	74·61 30·14		
Cl (C,H,..)							Cl (%)		
Chloroacetamide	C_2H_5ONCl	93·519	25·69	4·31	17·11	14·98	37·91		
1-Chloro-2,4-dinitrobenzene	$C_6H_3O_4N_2Cl$	202·563	35·58	1·49	31·60	13·83	17·50		
Hexachlorobenzene	C_6Cl_6	284·808	25·30				74·70		
Hexachlorocyclohexane	$C_6H_6Cl_6$	290·856	24·78	2·08			73·14		
Tetrachloro-*p*-benzoquinone (chloranil, tetrachloroquinone)	$C_6O_2Cl_4$	245·894	29·31		13·01		57·68		
Br (C,H,..)							Br (%)		
p-Bromoacetanilide	C_8H_8ONBr	214·076	44·88	3·77	7·47	6·54	37·33		
2,4,6-Tribromophenol	$C_6H_3OBr_3$	330·838	21·78	0·91	4·84		72·47		

I ($C_xH_y..$)							I (%)		
Erythrosin (iodeosin, 2,4,5,7-tetraiodofluorescein)	$C_{20}H_8O_5I_4$	835·924	28·74	0·96	9·57		60·73		
o-Iodobenzoic acid	$C_7H_5O_2I$	248·027	33·90	2·03	12·90		51·17		
S ($C_xH_y..$)							Cl (%)		
S-Benzylthiuronium chloride	$C_8H_{11}N_2ClS$	202·715	47·40	5·47		13·82	17·49	15·82	
Sulphanilamide	$C_6H_8O_2N_2S$	172·212	41·85	4·68	18·58	16·27		18·62	
Sulphanilic acid (anhydrous)	$C_6H_7O_3NS$	173·196	41·61	4·07	27·71	8·09		18·51	
Sulphonal	$C_7H_{16}O_4S_2$	228·337	36·82	7·06	28·03			28·09	
Thiourea	CH_4N_2S	76·125	15·78	5·30		36·80		42·12	
P, As ($C_xH_y..$)									As (%)
o-Arsanilic acid (*o*-aminophenylarsonic acid)	$C_6H_8O_3NAs$	217·048	33·20	3·72	22·11	6·45			34·51
									P (%)
5-Chloro-4-hydroxy-3-methoxybenzyl isothiourea phosphate*	$C_9H_{14}O_6N_2ClSP$	344·725	31·36	4·09	27·85	8·13	10·29	9·30	8·99
Triphenylphosphine	$C_{18}H_{15}P$	262·293	82·43	5·76					11·81
Me ($C_xH_y..$)									Ca (%)
Calcium oxalate	C_2O_4Ca	128·102	18·75		49·96				31·29
Phenylmercuric acetate	$C_8H_8O_2Hg$	336·762	28·53	2·39	9·50				Hg (%) 59·57
Potassium acid phthalate	$C_8H_5O_4K$	204·228	47·05	2·47	31·34				K (%) 19·15
Sodium oxalate	$C_2O_4Na_2$	134·004	17·93		47·76				Na (%) 34·31

* W. H. Smith. *Anal. Chem.*, **30**, 149 (1958).

Notes

For the calculation of molecular weights and percentages, the atomic weights used are those proposed by the Commission on Atomic Weights of the I.U.P.A.C., 1957.

The percentage figures are given to the second decimal. Where the third decimal is less than 0·005, the last figure has been disregarded. Where the last figure has been rounded off, it has been underlined (0·375 = 0·38).

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SECTION OF ANALYTICAL CHEMISTRY

COMMISSION ON OPTICAL DATA*

REPORT ON CALIBRATION OF WAVELENGTH AND PHOTOMETRIC SCALES OF NON-RECORDING SPECTROPHOTOMETERS

A. C. Menzies

1. INTRODUCTION

The spectrophotometer is an instrument which is used to measure the intensity of a beam of light for a narrow range of wavelengths. There are, therefore, two principal quantities to be determined:

(a) the region of wavelengths, which is a dispersion problem, and

(b) the intensity of the beam, which is a photometric problem.

These two are connected. There may be errors in the measurement of both quantities. There may be an error in the reading of the wavelength scale, and, as a result of this, the intensity which is measured at the spurious wavelength is incorrect. The actual measurement of intensity may be subject to an error, owing to the photometric means employed. It follows that the permissible error in wavelength reading is that which causes an error in intensity determination not greater than that which the photometric measurement entails. Thus the two quantities are connected through their respective errors, which should be matched. Nevertheless, it is permissible and convenient to consider them separately, and this will now be done, after defining the terms which are used.

Because of their widespread use, the spectrophotometers considered in this report will, unless otherwise stated, be of the photoelectric non-recording type. The report envisages the employment of such instruments as being the normal one of measuring absorption only. The purpose may be:

(a) analysis of samples, by measurement of their absorption (the purpose with which this report is mainly concerned),

(b) determination of structure of compounds,

(c) measurement of the intensity of the radiation transmitted.

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These may be further broken down; for example, under (a) one may wish to measure the absorption of a sample over a wide range of wavelengths, or may wish to determine very accurately the absorption in a few wavelength regions. Further, one may wish to measure a small change in absorption in one particular spectral region, due to changes in other parameters such as temperature, dilution and so on. According to the nature of the problem, the error which can be tolerated in wavelength or intensity reading varies in magnitude.

2. NOMENCLATURE

2.1—In a preliminary version of this report, attention was drawn to the chaotic state of the nomenclature of absorption spectrophotometry, and the writer suggested that the Commission should consider this and make recommendations. This was done at a meeting in Liège in 1958. Since the agreed terminology is used in this report, the conclusions are here reported. (In the meantime, this question was also examined by the Commission on Molecular Structure and Spectroscopy and its decisions were reported in *Information Bulletin* No. 8. An examination of both sets of decisions shows them to be in practically complete agreement, the only difference being that some extra terms were agreed by the Commission on Optical Data. To distinguish them, they are put in square brackets in the following list.)

2.1.1—The unit of wavelength is the ångström (Å); the millimicron (mμ) is usable when appropriate to the coarseness of the instrument being used. [The term nanometer (nm) is recognized as synonymous with millimicron, and is helpful when a typewriter is used.]

2.1.2—The symbol of wavelength is λ.

2.1.3—Concentrations (c) are expressed in moles/litre.

2.1.4—Sample thickness (b) is expressed in centimetres. The symbol l is not liked, since it may easily be confused with the digit 1.

2.1.5—Incident and emergent intensities are written as I_0 and I respectively. [Φ_0 and Φ for these quantities are tolerated.]

2.1.6—The extinction coefficient, ϵ_λ, is such that

$$\epsilon_\lambda = \frac{\log_{10}(I_0/I)_\lambda}{cb}$$

the units being (cm mole/litre)$^{-1}$.

2.1.7—[The quantity $\log_{10}(I_0/I)$ is known as the absorbance, A. The expression optical density and the symbol D are also recognized.]

2.2—To make clearer the meaning of these terms, consider the measurement of the absorption of a solution placed in a cell in the dispersed beam issuing from a monochromator. Suppose that immediately after entering the liquid the beam has intensity I_0, and contains wavelengths over a range $\delta\lambda$, the mean wavelength being λ. The beam traverses a path of

length b in the solution, and the intensity of the beam is then I. It will have decreased exponentially because of the absorption, so that

$$I = I_0 \times 10^{-ebc}$$

Hence the form given in **2.1.6.** It is important to consider the incident beam immediately after first entering the solution, so as to avoid complicating the definitions by considerations of the reflection losses at the walls of the cell, and absorption in the cell wall.

3. THE WAVELENGTH SCALE PROBLEM

3.1—If the sample has a small variation in absorption with wavelength, the wavelength reading need not be precise, but if a material such as a didymium salt is the sample a small error in wavelength setting may have a large effect on the apparent absorption.

3.2—Testing the scale

The simplest way to test the wavelength scale in the visible region is to use a line spectrum, such as is provided by a mercury lamp. With a narrow entrance slit, reduced to the stage when further reductions in width reduce brightness without reducing the apparent width of the line seen at the exit slit, and with the exit slit set so as just to embrace the spectral line, the wavelength indication should be that of the mercury line being examined. If now the slits (assumed symmetrical) are widened to the extent customary in the use of the instrument, the reading should remain the same, unless the prism is not being used at minimum deviation. With a wide entrance slit and the prism off minimum deviation, rays from one edge of the slit fall on the prism in a direction nearer to that of minimum deviation than rays from the other edge. Consequently, the deviation of the rays is not symmetrical about the mid-position, so that the mean wavelength changes as the slit is opened, when one considers a continuous source. Fortunately, most of the spectrophotometers under consideration use a Littrow system, in which the line under examination is produced by rays which pass through the prism close to the direction of minimum deviation. For radiation in the ultra-violet region, similar observations can be made when a screen of fluorescent material, such as uranium glass, is placed over the slit.

Wavelengths suitable for the purpose are given in *Table 1*, at the suggestion of M. Loeuille of Paris, who supplied the author with a list. This list has been modified and extended, and the suitability of the lines included has been specially checked in the author's laboratory. Some lines which might have been expected to be included have been omitted, either because they are susceptible to self-reversal (for instance, Hg 2537), or because other strong lines are so close that in an instrument with low dispersion the wavelength would be in doubt. The wavelengths (with the exception of the first line), are taken from Harrison's tables, and are given in ångströms, to the first decimal figure. They should be rounded off to the degree warranted by the precision of the instrument used (four significant figures for most instruments, three for the coarse ones). The fifth figure has been included so as to provide for greater resolution possible in the future. It

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is not necessary to have all the sources listed, unless a very detailed calibration is required; for most workers a (low-pressure) mercury lamp will suffice. A neon lamp is useful if the visible range is especially important.

Table 1. Useful spectral lines for wavelength calibration (in Å)

Mercury	*Neon*	*Helium*	*Rubidium*	*Zinc*	*Cadmium*
1942·3	5330·8	3888·6	4201·9	2025·5	2677·6
2302·1	5341·1	4471·5	4215·6	2061·9	3261·1
2378·3	5400·6	4921·9	5578·8	3282·3	3403·7
2446·9	5852·5		7800·2		3610·5
2752·8	5944·8	*Sodium*	7947·6	4680·1	4678·2
2803·5	6143·1			4722·2	4799·9
2893·6	6334·4	5682·7	*Caesium*	4810·5	5085·8
3125·7	6402·2	5688·2		6362·3	6438·5
3906·4	6678·3	5890·0	4555·4		7346·2
4046·6	6929·5	5895·9	4593·2	*Hydrogen*	
4077·8	7173·9		8521·1		*Thallium*
4358·4	7245·2	*Potassium*	8943·5	4101·7	
5460·7				4340·5	2767·9
5769·6	*Krypton*	4044·1	*Argon*	4861·3	2918·3
5790·7		4047·2			3229·8
	4274·0	7664·9	8115·3		3519·2
	8928·7	7699·0			3775·7
					5350·5

3.3—Sometimes the exit slit is opened wide, and a transparent plate carrying cross-wires is placed over it with the mid-point of the cross-wires half-way between the jaws. The entrance slit is made narrow and the spectral line is moved into coincidence with the cross-wires. For the ultra-violet region, a uranium glass plate with cross-wires is used. Such a method requires the exit and entrance slits to be independently adjusted.

3.4—An alternative procedure uses the method of paragraph **3.2**, substituting the electrical measuring system for the eye, and seeking for a maximum emission. This method is to be preferred to the foregoing ones, since with prism instruments the spectral line is curved, so that the electrically effective position of the line with regard to the exit slit is not quite the same as that of the middle of the line. In principle the best method is likely to be that one which most nearly follows the procedure necessary in using the instrument in the normal way. According to this principle this electrical method is to be preferred.

3.5—Interference method

A different approach is to use Edser–Butler fringes[1] to produce maxima and minima in the spectrum of a continuous source. This has been used by Rank, Rix and Wiggins[2] for calibration of absorption spectra and applied to the calibration of spectrophotometers by Heidt and Bosley[3]. Rank *et al.* used bare glass plates, to which the simple theory applies, *viz.* $P\lambda = zt$, where P is the order of interference and t is the geometrical separation of the plates. Heidt and Bosley used aluminized surfaces to increase the

reflectivity, but do not appear to have made the correction for the phase change on reflection at the metal surfaces. This may make a difference of several ångströms when carrying over to 2000 Å an effective gap separation determined at 3500 Å, for gaps as small as those actually used (of the order of 10^{-3} cm). Heidt and Bosley obtained absorbance wave curves by placing a narrow-gap étalon in the sample compartment of the spectrophotometer, and standardized the gap by superposing the record of the hydrogen lines occurring in the lamp used for the ultra-violet. From this, estimates may be made of the positions of the maxima and minima, and these were used to check the wavelength scales. If found necessary, a calibration curve can be constructed.

Buc and Stearns[4] used an analogous device which produced interference fringes by polarization with a retarding plate. If a medium other than air is used, the dispersion of the medium must be taken into account.

4. EFFECTS DUE TO FINITE WIDTH OF SLITS

As customarily used, the slits of the spectrophotometer may have to be wide, so that sufficient energy reaches the detector. Used in conjunction with a source of continuous radiation, the exit slit will pass light having a range of wavelengths. The range will be greater, the wider the slits and the less the dispersion of the instrument. It may also be impure, in the sense that radiation of very different wavelengths is present owing to stray light—this is considered in paragraph **5** below.

4.1—Width of band of wavelengths passed. (Diffraction ignored)

Suppose F_1 and F_2 are the focal lengths of the collimator and " camera " lenses respectively. Imagine a finite entrance slit, of width W_1 and a narrow exit slit. If D is the angular dispersion $(d\theta/d\lambda)$, $W_1/F_1 = D\delta\lambda$, so that the band of wavelengths emerging through the narrow exit slit is given by

$$\delta\lambda = W_1/F_1D$$

Suppose now that the exit slit is widened to W_2. Considering rays from the extreme edges of W_1, it will be seen that the band now emerging from the exit slit is of width $\Delta\lambda$ given by

$$\Delta\lambda = W_1/F_1D + W_2/F_2D$$

As normally used, the width W_2 of the exit slit is matched to the width W_1 of the entrance slit, so that $W_1/F_1 = W_2/F_2$ and

$$\Delta\lambda = 2W_1/F_1D = 2W_2/F_2D$$

$\Delta\lambda$ here is the complete range of wavelengths passed, without reference to the flux associated with the different wavelengths.

4.2—Effect of diffraction

If a narrow entrance-slit is illuminated by a monochromatic source of wavelength λ, there will be a widening of the line-image due to diffraction.

If B is the breadth of the beam of light emerging from the prism, then the (half)-width W_d of the flux wavelength plot is given by

$$W_d = \lambda F_2 / B$$

if a square cross-section is assumed for this beam. If the entrance slit is now opened, so that the *image* of this in the plane of the exit slit is W_2, Kaiser and Hansen[5] have shown that the effective slit width W_{eff} is given sufficiently nearly by

$$W_{eff} = W_2(1 + W_d^2/W_2^2)^{\frac{1}{2}}$$

Thus, when the entrance slit is narrow, the effective width is mainly due to diffraction, while when the entrance slit is wide, the effect of diffraction becomes negligible. Applying these considerations to **4.1**, one arrives at

$$\Delta\lambda = W_{eff} D F_2$$

where $\Delta\lambda$ is the width of the waveband at half-intensity.

4.3—Variation of flux passed with wavelength

So far, only the wavelengths passed have been considered, without reference to the flux associated with each wavelength. Naturally this will depend upon the variation of flux with wavelength in the source, and various attempts have been made to consider the general case. For example a general treatment has been given by Hardy and Young[6], and Eberhardt[7] has considered the case of matching entrance and exit slits, with examples of application to particular absorption bands. For a detailed treatment of the waveband problem, see the paper by Perry[8].

For the purpose of this report, the ideal case may be considered of a waveband over which the flux associated with each wavelength is constant, and the dispersion is normal over the waveband. If diffraction is ignored, and the slits are matched, the extreme wavelengths will be associated with zero flux, while for the central wavelength the flux will be a maximum; the flux–wavelength plot is triangular.

If the exit slit is wider or narrower than the image of the entrance slit, the plot is trapezoidal; the flat top is of width $|(\delta\lambda)_2 - (\delta\lambda)_1|$, the base of width $(\delta\lambda)_2 + (\delta\lambda)_1$, where $(\delta\lambda)_2$ is the waveband corresponding to the actual exit slit, and $(\delta\lambda)_1$ is that covered by the image of the entrance slit. The half-flux width is seen to be either $(\delta\lambda)_2$ or $(\delta\lambda)_1$, whichever is the greater.

For the normal purposes of analysis with the spectrophotometers here considered, a triangular plot is sufficient.

It is to be noted that for matching slits the half-flux width, expressed in wavelengths, is the same as the total waveband passed when the exit slit is very narrow (ignoring diffraction).

For non-matching slits, starting from the condition of match, as the exit slit alone is progressively widened, the flux associated with particular wavelengths under the flat top is unaltered, but the total flux increases, as does also the width of the waveband. If from the state of matching,

the exit slit is progressively decreased, the total flux is reduced, without gain in purity. Consequently to match the slits is advantageous, unless the energy is insufficient.

5. STRAY LIGHT

5.1—In well designed spectrophotometers this should be negligibly small over the useful range of the instrument, if it is in good condition. If it is not well designed, or if the optics have been allowed to become dusty, light will be scattered in unwanted directions and some may emerge from the exit slit mixed with the wanted radiation. With continuous illumination, the ratio of stray light to wanted light is independent of slit width, but with monochromatic illumination, it is proportional to the slit width.

The effect of stray light is to give spuriously high or low transmittance, according as the absorbing substance has a higher or lower transmission for stray light than it has for the wanted light. Suppose T is the true transmittance of the sample for the wanted wavelength, and T_s is the true transmittance of the sample for the wavelength of the stray light. Let T_{app} be the apparent transmittance of the sample as measured in the presence of stray light. Let I_0 be the intensity of the incident beam of wanted wavelength, and S_0 be the intensity of the incident stray light.

Then $$T_{app} = (I_0T + S_0T_s)/(I_0 + S_0)$$

or $$T_{app} - T = S_0(T_s - T)/(I_0 + S_0)$$

So if $T_s > T$, $T_{app} > T$ and conversely.

Consequently if T is known, measurement of T_{app} with the spectrophotometer shows whether it is equal to T or greater or less. A special case could arise when the stray light had wavelengths belonging to two (or more) regions of the spectrum, of such a kind that apparently the true transmittance was measured, falsely. This, if suspected, could be shown up by measurements of different samples having absorption bands in different places.

Stray light is normally lower in systems employing double monochromators, and with single monochromators the right use of auxiliary filters may help in a similar way, by diminishing the intensity of unwanted wavelengths.

It is convenient to distinguish between two types of stray light, *viz.* that due to wavelengths far from the wavelength region wanted (" far " stray light) and that due to wavelengths close to the waveband being measured.

5.2—" Far " stray light

The simplest method of *detecting* such stray light, is to measure the apparent density of an absorbing substance in the wavelength region being investigated, and then to introduce into the path of the incident radiation an optical filter which transmits the region required, but obscures other regions. If the density now measured is different, some scattered radiation has been removed.

5.3—An estimate of the amount of stray light is sometimes made by using the formula of paragraph **5.1**, and putting T_s arbitrarily equal to unity, so that

$$T_{app} - T = S_0(1 - T)/(I_0 + S_0)$$

or

$$S_0/I_0 = (T_{app} - T)/(1 - T_{app})$$

A measurement of T_{app} is made of a substance for which T is known. Clearly this is no more than a rough estimate, for there is no justification for regarding T_s as unity. Unless the wavelength region of the stray light is known, a *measurement* cannot be made of the stray light in this way. A satisfactory method is given in paragraph **5.5** below. If a good double monochromator free from scattered light is available, light from this can be fed into the spectrophotometer under test, and the output can then be measured for different settings of the wavelength of the instrument under test. This has been done by Pritchard[9].

5.4—Another method of estimating stray light, described by Hogness, Zscheile and Sidwell[10], which does not require a substance of known density, can be applied when it is possible to increase the length of path through an absorbing liquid, or to increase the concentration. (The former is preferable, since the latter may cause a change in absorption due to factors affecting the validity of Beer's law.) If stray light is absent, the density will increase progressively, but if it is present, the density will rise to a maximum value, as $d = \log_{10}(I_0 + S_0)/(I + S)$ tends to $\log_{10}(I_0 + S_0)/S$.

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5.5—" Near " stray light

Stray light due to wavelengths near to those of the waveband being studied may be very troublesome, and it will not readily be detected by the foregoing methods. Preston[11] measured stray radiation by a technique which can measure both kinds of stray light. He assumed that the stray radiation illuminates both halves of the slit equally. The method is to fix a plate rigidly on the entrance slit so as to cover a little more than half its length. A similar plate is arranged to block *exactly* half the exit slit, the half being blocked corresponding to the image of the open half of the entrance slit. This plate may be put in position or removed at will. When the first screen only is in place, the wanted beam emerges from just less than half the exit slit, while scattered light fills the exit slit symmetrically. When the second plate is also in position, the wanted beam is eliminated and half the stray light emerges. The application of the method may be shown by considering the measurement of the true transmission of a filter (free of error due to stray light).

Four readings are taken, all with the plate on the entrance slit:

R_1	No screen on exit slit	No filter
R_2	No screen on exit slit	Filter in place
R_3	Screen on exit slit	Filter in place
R_4	Screen on exit slit	No filter

The apparent transmission of the filter will be R_2/R_1. The true transmission will be $(R_2 - 2R_3)/(R_1 - 2R_4)$. If these two are equal, there is no stray light. This method is unduly long for use as a routine, but it is recommended for detecting and measuring stray light if it is suspected. For this test, in the form presented by Preston, it is necessary that the exit and entrance slits should be separate.

Tunnicliff[12] has described a method of measuring near stray light, based on the use of the narrow absorption band in mercury vapour at 2537 Å. This becomes broader as the temperature of the vapour is raised.

Stray light has been examined theoretically by Perry[13] and some practical examples are considered by Holiday and Beaven[14].

6. THE INTENSITY SCALE PROBLEM

6.1—The photoelectric spectrophotometer is provided with a scale engraved in terms of optical density, transmittance, or both. It is required to know what confidence can be placed in the graduation, and if necessary what curve should be constructed to calibrate the readings. (The latter procedure is not recommended; it is better to change the offending component, probably photocell or potentiometer.) These requirements are met to a different extent by the following three types of method in general use, which may be distinguished as:

(a) *Physical absorption methods*, which employ diaphragms, polarizing arrangements and the like, simulating absorption of calculable amounts. Since the absorption is calculable, these are absolute methods.

(b) *Chemical absorption methods*, which employ absorption by solutions having "known" optical densities. Since one cannot calculate the optical densities, one must measure them on an already calibrated instrument. These are, therefore, comparative methods, which, however, are very convenient.

(c) *Electrical methods*—These are not absolute methods, in that, for example the linearity of the photocell must be assumed to be satisfactory, or be determined separately. They are extremely convenient, and if the instrument satisfactorily passes these tests it is almost certainly correct, for an unusual combination of circumstances is required to render them nugatory.

7. PHYSICAL ABSORPTION METHODS

7.1—Variable aperture

This method is extremely simple, but requires great caution in its application.

An aperture is easily made variable, and is placed in a beam which is made as uniform as possible over the whole cross-section of the aperture opened to the greatest area used. If the beam is uniform, then the flux passed will be directly proportional to the area of the opening. The image of the opening, when enlarged to the maximum used, must fall within the aperture stop of the instrument—otherwise at some point when it is being

opened, the relationship between flux and area will fail. Good homogeneity of the beam is easier to attain if the lens or mirror used to form the beam is used at a low relative aperture. Examples of the use of variable apertures are the Spekker photometer of Hilger and the Pulfrich photometer and Elko II of Zeiss.

7.2—Grids

The grids or gratings are formed for example from wire mesh, and allow light from different zones of the lens forming the beam to pass simultaneously. Each such grid has a fixed transmittance, and the grids are interchangeable. Unfortunately, owing to diffraction effects, grids are not neutral, having a different transmission for long waves than for short. They are convenient and do not easily suffer from ageing effects. The beam need not be as homogeneous as when the gross aperture type of attenuator is used.

Grids have been revived recently by Heidt and Bosley[3] who used screens of single strands of brass wire, made sufficiently small to be placed in the sample tray in the spectrophotometers they investigated. They used screens singly and in tandem, combining up to six screens, and naturally found that the relative orientation of screens in tandem had a marked influence. They found the density to be dependent on wavelength, and expressed this dependence by a formula. While this detracts in principle from the usefulness of such screens, they stated that the screens could be treated as neutral " in the first approximation ", by which they mean that " the uncertainties in the absorbance values in any case are no greater than those encountered in the use of potassium chromate " (see below).

(The calculated value of the percentage open area should be $(1 - ms)^2$, where m = mesh in number of wires per inch, and s = diameter of the " wire in inches ", and not as printed in the paper.)

A grid of special design due to Kaiser[15], which has several advantages over fixed screens, may be mentioned here. A plate is pierced with holes which are made with a precision drill, and the holes are opened out on each side of the plate so that they have the precise diameter half-way through the plate, but the thickness of the plate does not obstruct the angular aperture of each hole. The transmission may be calculated from the number and diameter of the holes. The plate has an oval rim, resting on two rollers; as the rollers rotate the plate " tumbles " in the beam, randomizing the positions of the holes.

7.3—Rotating sectors

7.3.1—*Simple type*—This is a rotating " chopper ", which consists of an opaque disc with a sector missing, so that in each period the light passes for a time depending upon the angle of the sector. The sector may be made to be adjustable, by superposing on the same axle two discs each with two 90° sectors missing, and adjusting one with respect to the other so that effective sector openings from 90° to zero may be obtained. For this purpose it is customary to mark a degree scale (or a percentage scale) on one of the opaque sectors. Since there are two openings, the transmission varies from 50 per cent to zero. It is also possible to have curved

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sectors, so that for example a logarithmic law may be followed. Such an attenuator operates not by reducing the intensity of the light, but by reducing the time during which it operates. Consequently errors will result if the period of flicker is not small compared with the time constant of the measuring circuit. Thus in practice such a device may only be used with an integrating device, or one having a long time constant. Success has been achieved with rotating sectors in photographic photometry, but this simple type is not suited to photoelectric spectrophotometers.

7.3.2—*Hollow axle rotating sector*—Pool[16] devised a special form of rotating sector which may be used with photoelectric spectrophotometers, to reduce the intensity in a calculable way. It reduces the intermittent effect in practice to a small amount—with perfect optics and adjustment it would be zero. The sector is mounted on a hollow axle supported by a ball-race round it, and it is driven by a belt, so that the whole beam passing through enters the spectrophotometer. The image of the sector is arranged to fall within the stop of the spectrophotometer. The writer introduced some modifications to Pool's form of the apparatus. In this a " lid " is placed on the rotating hollow cylinder. The lid is formed from a ring of stout metal which fits over the end of the hollow cylinder, with a sheet of metal screwed onto the ring. Consider an attenuation of one half. The semi-circular sheet of metal which forms the obscuring half needs only to have the edge straight which constitutes the diameter of the opening. This is adjusted by means of the screws, so that when the sector rotates, neither a black centre nor a white centre on a grey ground can be seen. It is very easy to secure this exact adjustment.

If the beam were completely homogeneous, then exactly half the intensity would be obtained (this would also be true if the sector were at rest). The effect of the rotation is to use different portions of the beam in turn. If the beam is not truly homogeneous, then there is an intermittent effect, but only in proportion to the degree of inhomogeneity of the beam. If the sector rotates rapidly enough, the intermittent effect is not harmful. With a photoelectric spectrophotometer there was no flicker of the meter needle to be seen. Openings of other sizes can be adjusted in a similar manner, but already much can be done with a half-intensity device, since one may arrange for any setting of the intensity scale to correspond to full opening of the sector, and then to read the half-value.

7.4—Polarization devices

With a pair of nicol prisms in series in the beam, one may reduce the intensity of the emergent beam in a calculable way by orienting the principal plane of one with an angle ϕ relative to that of the other, since the transmittance is proportional to $\cos^2\phi$. Such a device can only be used over the range of wavelengths transmitted, which in practice means the visible and near ultra-violet regions. (Polaroid is unsuitable because of the partial transmission in the violet and red of crossed polaroids.) The small aperture of the nicol also introduces a difficulty. If the density required is high, ϕ must be large, and since $\mathrm{d}I/I = 2 \tan\phi \mathrm{d}\phi$, a small error in adjusting ϕ leads to a very large error in intensity.

7.5—Neutral filters

If there were a strictly neutral filter, it would be possible to construct wedges of the material which could be used to calibrate the intensity scale. Actually no truly grey material has yet been made. For some purposes finely dispersed particles of such substances as carbon, or finely divided metals embedded in gelatine or glass, have been used. Partly exposed and developed photographic plates prepared with finely divided silver constitute such a filter in effect. They are not truly neutral, and have to be standardized in some way so that, though convenient in use, they are secondary standards, and should be calibrated for different wavelength regions. A good glass filter of this type serves as a convenient check to apply from time to time.

The interposition of a glass filter may introduce trouble due to light losses by reflection at the surfaces of the filter. Cary has greatly reduced this effect, by having a trough of liquid in place all the time, and introducing the filter by plunging it into the liquid (*e.g.*, oil). The liquid is chosen so as to have a refractive index sufficiently near that of the glass to give rise to little reflection at the liquid–glass interfaces.

7.6—Inverse square law of distance

Use may be made of this law for the satisfactory calibration of a filter to be used with a spectrophotometer, in the visible or ultra-violet regions, if certain precautions are taken. Kaiser[15] has described such a method, and the errors to be avoided. The lamp is placed in a light-tight housing, with a sharp-edged window. The light passes through suitably arranged windows and falls on a flat surface, coated with magnesium oxide. The distance between this surface and the lamp may be varied, so as to vary the intensity of illumination of the surface in a calculable way. The light must not be allowed to fall directly on the receiver, first because the cathode of a photocell or photomultiplier is insufficiently flat, and secondly because trouble may be caused by shading, *e.g.*, by anode wires. This may be avoided by introducing an integrating sphere (see also Grossmann, Sawyer and Vincent[17]).

8. CHEMICAL ABSORPTION METHODS

These employ solutions of definite composition, concentration and thickness, for which the optical density is believed to be known. The absorbing material must be easily obtained in a pure state, and have absorption bands which are flat-topped—*i.e.*, have maxima (or minima) of absorption which change only slowly with change in wavelength (otherwise the error in photometry may be affected by error in the wavelength scale). If an error in the wavelength scale is suspected, the measurement of density may be made at the maximum (or minimum) density. A good example of the use of this method is the comparative tests carried out by the British "Photoelectric Spectrometry Group"[18, 19], which stimulated the setting up afterwards of similar tests by the Dutch "Werkgroep Voor Photoelectricshe Spectrophotometrie"[20]. These show that with normal care, in most chemical laboratories a reproducibility of about 1·5 per cent

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may be achieved. With considerable care, especially giving attention to cleanliness, and measuring the absorption at an agreed temperature of the liquid, it should be possible greatly to reduce this (see, for example, the work of Haupt[21]). Collaborative tests in America have been reported by Brode, Gould, Whitney and Wyman[22], by Vandenbelt[23] and by Vandenbelt and Spurlock[24]. A discussion of collaborative tests has been published by Cahn[25], and Gridgeman[26] has given a general discussion of the reliability of spectrophotometry.

9. ELECTRICAL METHODS

9.1—In the *making* of photoelectric spectrophotometers, the simplest way of ensuring an optical density scale accurate within the tolerance designed, is to select photocells which are sufficiently linear in the light-intensity–current characteristic (fortunately, this is easy), and to select potentiometers and fixed resistors having resistances within the tolerances calculated as being necessary to obtain the overall accuracy. (No compensatory design is practical because of the possibility of spares being required.) The linearity of the photocell guarantees that potentials developed across a fixed resistor will be proportional to the light fluxes received, and the linearity of the measuring potentiometer ensures that potentials will be accurately determined by the reading of the scale attached to the potentiometer. The spectrophotometer of the type being considered is a potential-comparing device, using a resistance bridge. When the potentiometers are checked for errors, the errors found in rejected potentiometers are random. It is likely, therefore, that the photocells in the instrument are sufficiently linear, and that if the potentiometer is faulty the errors are random.

9.2—Single filter method

This is a very simple test to apply, and if the instrument fails on this test there is certainly something wrong. If it does not fail on this test, then the instrument is proved reliable, *unless* (as pointed out by Cannon[27]), the photocell has a current characteristic proportional to a power of the light-intensity ($i \propto I^n$). So far, in the author's experience, this has not occurred within the current range used in these spectrophotometers so that in practice the test may be relied upon. If there should be doubt on the linearity of the photocell, measurement of the optical density of a single standardized filter should dispel it, since the optical density will be measured as nd for the law just considered and the correct results will only be obtained if $n = 1$.

With the scale reading 100 per cent transmission, and no filter in the way, the meter needle is balanced with the 100 per cent adjustment. The filter is now inserted, and the transmission (say x per cent) determined in the ordinary way. This is now repeated, with the photometer scale at some other reading, *e.g.*, m per cent, at the commencement, and the needle is balanced. The filter is inserted again, and a new transmission determined, which should read $mx/100$ per cent if the scale is correctly calibrated. This can be repeated for various values of m. A good procedure is to use as a

filter a trough of absorbing solution, with a trough containing solvent only for comparison. This follows closely the normal use of the instrument.

The simplest procedure is to work with density readings, naturally commencing with the normal use of the 100 per cent setting knob (" check " knob) to obtain density zero. Insertion of the solution gives a reading of *a*. Now the check knob is set in such a position that with the solvent trough in place, balance is obtained for a reading *a*. Replacement of the solvent by the solution will now yield a new density reading, *b*. The process is repeated, now starting with *b*. If the instrument is properly calibrated, the readings *a*, *b*, *c*, *etc.*, should form a series in arithmetical progression.

As an example the figures in *Table 2* are given. They were obtained by the writer in checking an instrument, with potassium dichromate solution against water, for wavelength 313 mμ.

Table 2. Scale readings

With water	*With solution*	*Calculated series*
0·000	0·124	0·1243
0·124	0·249	0·2486
0·249	0·373	0·3729
0·373	0·496	0·4972
0·496	0·621	0·6215
0·621	0·745	0·7458
0·745	0·870	0·8701

The figures in the first two columns will be seen to be in arithmetical progression, being approximately multiples of 0·1234. Incidentally, the biggest error in this test where the reading was 0·496, corresponded to an error in transmittance of one-quarter per cent.

9.3—Two-filter method

A variant subject to the same proviso as in paragraph **9.2** is to use two filters, measure the density of each separately, and then measure the density of the two combined. Since this should be the sum of the two densities measured separately, the calibration of the scale can be checked. The procedure may be repeated as before, with intial balancing at different positions on the scale, or by keeping the initial setting as 100 per cent transmission, and using different filters.

9.4—Added light method

Hansen[28] describes a difference method which uses a similar principle, namely that the response to two sources simultaneously should be the sum of the responses to the two sources separately. The special feature is that he adds a constant small light-flux from a second lamp (of constant output) after each reading, and reads the new deflection of the meter. If the instrument is correctly calibrated, the increment of reading should be the same. This method is not subject to the proviso of paragraph **9.2**, *i.e.*, the response of the detector may be any function of the incident light-flux.

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10. PREFERRED METHODS

When several good methods of test are available, the writer prefers that which most nearly follows the natural procedure in using the instrument. For testing wavelength scale calibration, therefore, he prefers the method of paragraph **3.4**, and for testing photometric scale calibration one of the methods of paragraph **9**.

11. NOTE ON CLEANLINESS

Though not strictly within the scope of this report, it is not possible to lay enough stress on the need for scrupulous cleanliness if consistent results are to be obtained. Professor Pestemer of Leverkusen keeps his cells when not in use in a liquid, so that the inner cell walls are never dry, and the cells can be flushed out before use.

12. NOTE ON EFFECT OF TEMPERATURE

It is not always realised that the temperature coefficient of absorption may be high enough to falsify the observations, particularly when accurate results are needed. This may account for some part of the discrepances observed in collaborative tests (see paragraph **8**). Haupt[21] (*loc. cit.*, p. 445) measured the transmission of an alkaline solution of potassium chromate over a range of temperature of 25°C, and gives detailed observations. The results appear to indicate that the absorption bands move towards longer wavelengths with increase in temperature.

13. NOTE ON ABSORPTION CELLS

Each cell must have parallel walls, and pairs of matched cells should be truly matched. A test of this matching can be made by making an observation in the usual manner, and then a further observation after interchanging the contents of the respective cells. Care should be taken that the cells are placed with their walls perpendicular to the light beam. If the normal to the cell walls makes an angle θ with the light beam, and the thickness of the cell is b, then the path through the cell is now $b' = b \sec \theta/\mu$, where μ is the refractive index of the contents. This makes the fractional error in path $(b' - b)/b$ equal to $\theta^2/2\mu^2$, and this is the same as the fractional error in optical density which can be tolerated. For aqueous solutions, and an error of one part in a thousand, this necessitates an accuracy of setting of about 3°, which is easy to achieve.

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SECTION OF ANALYTICAL CHEMISTRY

COMMISSION ON ELECTROCHEMICAL DATA

and

SECTION OF PHYSICAL CHEMISTRY

COMMISSION ON PHYSICO-CHEMICAL SYMBOLS AND TERMINOLOGY

REPORT ON THE STANDARDIZATION OF pH AND RELATED TERMINOLOGY*

R. G. Bates and E. A. Guggenheim

The standardization of pH has been achieved in Great Britain[1], in the United States[2–5], and recently also in Japan[6]. In their essential elements, the three standards are in agreement; only differences of detail exist. It is the object of this report to summarize, for the information of all national groups interested in pH, the extent of standardization already achieved and to indicate how this area of agreement could perhaps be extended to other conceptions related to pH.

1. SYMBOLS

There already exists international agreement that pH should be written and printed on line in roman type. We recommend that, with the unique exception of pH, the operator p (printed in roman) should denote $-\log_{10}$. For example

$$\mathrm{p}m_{\mathrm{H}} \quad \text{means} \quad -\log_{10} m_{\mathrm{H}}$$

$$\mathrm{p}m_{\mathrm{H}}\gamma_{\mathrm{H,Cl}} \quad \text{means} \quad -\log_{10}(m_{\mathrm{H}}\gamma_{\mathrm{H,Cl}})$$

$$\mathrm{p}m_{\mathrm{H}}\mathring{\gamma}_{\mathrm{H,Cl}} \quad \text{means} \quad -\log_{10}(m_{\mathrm{H}}\mathring{\gamma}_{\mathrm{H,Cl}})$$

where m denotes molality and γ denotes mean activity coefficient (molality scale).

* Comments should be sent to Dr R. G. Bates, National Bureau of Standards, Washington, 25, D.C., U.S.A., or to Professor E. A. Guggenheim, Department of Chemistry, The University, Reading, U.K.

2. DEFINITION OF pH

In all three existing national standards the definition of pH is an operational one. The electromotive force E_X of the cell

$Pt,H_2|$ solution X | concentrated KCl solution | reference electrode

is measured and likewise the electromotive force E_S of the cell

$Pt,H_2|$ solution S | concentrated KCl solution | reference electrode

both cells being at the same temperature throughout and the reference electrodes and bridge solutions being identical in the two cells. The pH of the solution X, here denoted by pH(X), is then related to the pH of the solution S, here denoted by pH(S), by the definition

$$\mathrm{pH(X)} - \mathrm{pH(S)} = \frac{E_X - E_S}{(RT\ln 10)/F}$$

where R denotes the gas constant, T the absolute temperature, and F the faraday. In this equation the numerator and denominator must be expressed in the same units so that the pH difference here defined is a pure number.

The hydrogen electrodes in both cells may be replaced by identical hydrogen-ion-responsive electrodes, *e.g.*, glass or quinhydrone.

The two bridge solutions may be of any molality not less than about 3·5, provided they are the same.

3. STANDARDS

The difference between the pH of two solutions having been defined as above, the definition of pH can be completed by assigning a value of pH at each temperature to one chosen solution called the primary standard. In the British and Japanese Standards this is the definition of pH, the primary standard being a one-twentieth molar solution of pure potassium hydrogen phthalate. The pH of this solution is defined as having the value 4 exactly at 15°C. At any other temperature t°C between 0°C and 60°C its pH is defined by

$$\mathrm{pH} = 4{\cdot}00 + \frac{1}{2}\left(\frac{t-15}{100}\right)^2$$

This formula is for all practical purposes equivalent to one given elsewhere[7]. The question how this formula might be extended to temperatures higher than 60°C has been raised but not yet formally answered. The American Standard described below is in practically complete agreement with

$$\mathrm{pH} = 4{\cdot}00 + \frac{1}{2}\left(\frac{t-15}{100}\right)^2 \qquad 0 \leqslant t \leqslant 55$$

$$\mathrm{pH} = 4{\cdot}00 + \frac{1}{2}\left(\frac{t-15}{100}\right)^2 - \frac{t-55}{500} \qquad 55 \leqslant t \leqslant 95$$

The American Standard specifies four standard solutions with pH values specified at each temperature covering the range of pH from 2 to 12. These are given in *Table 1**.

There is a proposal to add as secondary standards 0·05 molar potassium tetroxalate (pH ≃ 1·7) and saturated calcium hydroxide (pH ≃ 12).

*Table 1**

t (°C)	*KH tartrate* (*satd at 25°C*)	0·05 *KH phthalate*	0·025 KH_2PO_4 + 0·025 Na_2HPO_4	0·01 *Borax*
0	—	4·01	6·98	9·46
5	—	4·01	6·95	9·39
10	—	4·00	6·92	9·33
15	—	4·00	6·90	9·27
20	—	4·00	6·88	9·22
25	3·56	4·01	6·86	9·18
30	3·55	4·01	6·85	9·14
35	3·55	4·02	6·84	9·10
40	3·54	4·03	6·84	9·07
45	3·55	4·04	6·83	9·04
50	3·55	4·06	6·83	9·01
55	3·56	4·07	6·84	8·99
60	3·56	4·09	6·84	8·96
70	3·58	4·12	6·85	8·93
80	3·61	4·16	6·86	8·89
90	3·65	4·20	6·88	8·85
95	3·68	4·23	6·89	8·83

* All concentrations are quoted in moles/litre of solution.

If the definition of pH in section **2** is adhered to strictly, then the pH of a solution might be slightly dependent on which standard solution was used. In fact any such variation is too small to be of practical significance. Moreover the American acceptance of several standards allows the use of the following alternative definition of pH. The electromotive force E_X of the cell

$$\mathrm{Pt,H_2}\,|\,\text{solution X}\,|\,\text{concentrated KCl solution}\,|\,\text{reference electrode}$$

is measured, and likewise the electromotive forces E_1 and E_2 of two similar cells with the solution X replaced by the standard solutions S_1 and S_2 such that the E_1 and E_2 values are on either side of, and as near as possible to, E_X. The pH of solution X is then obtained by assuming linearity between pH and E, that is to say

$$\frac{\mathrm{pH(X)} - \mathrm{pH(S_1)}}{\mathrm{pH(S_2)} - \mathrm{pH(S_1)}} = \frac{E_X - E_1}{E_2 - E_1}$$

This procedure is in fact useful and especially recommended when the hydrogen-ion-responsive electrode is a glass electrode.

This completes our report on the definition and measurement of the experimental quantity pH, of which the value depends on molalities, activity coefficients and transference numbers of the ions present.

The rest of this report is concerned with the interpretation of pH values as approximations to thermodynamical quantities.

4. IONIC ACTIVITY COEFFICIENTS

As a prelude to our discussion of the interpretation of pH it is expedient to say something about ionic activity coefficients. For the sake of brevity we shall restrict our detailed discussion to solutions containing only 1–1 electrolytes. The extension of the discussion to the more general case would require more complicated formulae without any new physical principles.

Electromotive force measurements on cells without liquid–liquid junctions (or other less direct experimental techniques) lead to experimental values of mean activity coefficients of an electrolyte but not to ionic activity coefficients. In particular the electromotive force of the cells

$$\mathrm{H_2,Pt} \mid \begin{matrix}\text{solution containing} \\ \mathrm{H^+ \text{ and } Cl^-}\end{matrix} \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

leads directly to the value of $m_{\mathrm{H}}m_{\mathrm{Cl}}\gamma^2_{\mathrm{H,Cl}}$ and, if the value of m_{Cl} is known, indirectly to that of $m_{\mathrm{H}}\gamma^2_{\mathrm{H(Cl)}}$.

It is permissible, and often convenient, to write conventionally

$$\begin{aligned}\gamma^2_{\mathrm{H,Cl}} &= \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}} \\ \gamma^2_{\mathrm{Na,Cl}} &= \gamma_{\mathrm{Na}}\gamma_{\mathrm{Cl}} \\ \gamma^2_{\mathrm{K,Cl}} &= \gamma_{\mathrm{K}}\gamma_{\mathrm{Cl}}\end{aligned}$$

and so on, but the values of the ionic activity coefficients γ_{H}, γ_{Na}, γ_{K}, γ_{Cl} are not uniquely defined. In each solution an arbitrary value may be assigned to the γ of any one chosen ionic species. This does not mean that one convention may not be more convenient than another. In particular all 1–1 electrolytes present in a solution of total molality less than 0·01 have, to an accuracy sufficient for most purposes, equal mean activity coefficients. Under these conditions it is natural to equate the ionic activity coefficients to the common mean activity coefficient; in fact any other convention would be far-fetched.

At higher molalities different electrolytes in the same solution have different mean activity coefficients and consequently the convention must be less simple. The following convention was described by one of us many years ago[9]. If we use M to denote a cation and X an anion, then

$$\frac{\gamma_{\mathrm{H}}}{\gamma_{\mathrm{M}}} \equiv \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{X}}}{\gamma_{\mathrm{M}}\gamma_{\mathrm{X}}} \equiv \frac{\gamma^2_{\mathrm{H,X}}}{\gamma^2_{\mathrm{M,X}}}$$

is thermodynamically well defined as is, of course, $\gamma_{\mathrm{M}}\gamma_{\mathrm{X}} \equiv \gamma^2_{\mathrm{M,X}}$. The convention for defining γ_{H} is

$$\ln\gamma_{\mathrm{H}} = \frac{\Sigma_{\mathrm{M}}m_{\mathrm{M}}\ln(\gamma_{\mathrm{H}}/\gamma_{\mathrm{M}}) + \Sigma_{\mathrm{X}}m_{\mathrm{X}}\ln(\gamma_{\mathrm{H}}\gamma_{\mathrm{X}})}{\Sigma_{\mathrm{M}}m_{\mathrm{M}} + \Sigma_{\mathrm{X}}m_{\mathrm{X}}}$$

with the analogous definition for a typical anion, say $\mathrm{Br^-}$:

$$\ln\gamma_{\mathrm{Br}} = \frac{\Sigma_{\mathrm{M}}m_{\mathrm{M}}\ln(\gamma_{\mathrm{M}}\gamma_{\mathrm{Br}}) + \Sigma_{\mathrm{X}}m_{\mathrm{X}}\ln(\gamma_{\mathrm{Br}}/\gamma_{\mathrm{X}})}{\Sigma_{\mathrm{M}}m_{\mathrm{M}} + \Sigma_{\mathrm{X}}m_{\mathrm{X}}}$$

These conventional relations automatically satisfy the thermodynamic requirement

$$\ln\gamma_{H} + \ln\gamma_{Br} = 2\ln\gamma_{H,Br}$$

When there is only a single electrolyte present, say HBr, these conventions reduce to

$$\ln\gamma_{H} = \ln\gamma_{Br} = \ln\gamma_{H,Br}$$

This convention is the simplest possible which treats all ionic species on a par. It is, in our opinion, aesthetically satisfying, but it has little practical utility because the values of all the mean activity coefficients of the several electrolytes present are usually not known. (In the more general case of ions with various charges the formulae are more complicated.)

We are therefore driven to using a much simpler, though less symmetrical convention. One that has proved especially useful is to define the activity coefficient of the *chloride* ion, at an ionic strength I not exceeding 0·1, by

$$\log\gamma_{Cl} = -\frac{AI^{\frac{1}{2}}}{1 + \rho I^{\frac{1}{2}}}$$

where A has at each temperature the value given by the theory of Debye and Hückel and ρ has a specified value; that recommended is $\rho = 1{\cdot}5$ mole$^{-\frac{1}{2}}$ kg$^{\frac{1}{2}}$.

Once the value of the activity coefficient of the chloride ion has been conventionally defined, this value may be combined with the value of $m_{H}\gamma^{\circ}_{H,Cl} = m_{H}\gamma_{H}\gamma_{Cl}$ to obtain a value of $m_{H}\gamma_{H}$ or of $pm_{H}\gamma_{H} = -\log_{10}m_{H}\gamma_{H}$.

5. pH OF STANDARD SOLUTIONS

We have stated that pH values have been assigned to four standard solutions in the American Standard and to one of these in the British and Japanese standards. We have as yet said nothing of how these values were chosen. They are in fact defined for each standard solution S by

$$pH(S) = pm_{H}\gamma_{H}$$

where the quantity on the right is determined according to the convention of section **4**.

6. APPROXIMATE INTERPRETATION OF pH

As a consequence of the relation

$$pH = pm_{H}\gamma_{H}$$

defining the pH of standard solutions, it can be verified that this same relation holds with an accuracy of $\pm 0{\cdot}02$ or better for all aqueous solutions of total ionic strength not exceeding 0·1, provided the pH lies between 2 and 12. Outside this pH range a more complicated recipe would be needed in any attempt to correlate pH with $pm_{H}\gamma_{H}$.

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7. THE ABBREVIATION pa_H

Some people may wish to abbreviate $pm_H\gamma_H$ (as conventionally defined in section **4**) to pa_H. Other people have strong objections to this notation because it may revive controversies of the days before the nature of pH was properly understood.

March, 1959

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SECTION OF ANALYTICAL CHEMISTRY

COMMISSION ON MICROCHEMICAL TECHNIQUES*

TERMINOLOGY FOR SCALES OF WORKING IN MICROCHEMICAL ANALYSIS

The Commission on Microchemical Techniques recommends the following classification of scales of working in chemical analysis in order to help to remove the existing confusion, particularly in the designation of methods involving less than 1 mg of sample.

* M. Zacherl (Austria), A. A. Benedetti-Pichler (U.S.A.), H. Malissa (Germany), J. A. Kuck (U.S.A.), D. Monnier (Switzerland), C. L. Wilson (U.K.).

Dénomination de méthode de travail / *Designation of working method*		*Masse de la quantité globale de substance mise en œuvre* / *Total sample amount* (g)	*Volume de la quantité globale* / *Total volume* (ml)	*Rapport à la quantité de " macrométhode "* / *Ratio to " macromethod "*
Actuelle / *Present*	*Proposée* / *Proposed*			
Macrométhode ou méthode classique Macro or classical method	Méthode grammique Gram method	$x \times 10^{0}$—$x \times 10^{-1}$	$x \times 10^{1}$—$x \times 10^{2}$	1
Semimicrométhode Semimicro method	Méthode centigrammique Centigram method	$x \times 10^{-2}$	$x \times 10^{0}$	1 : 10^{2}
Microméthode Micro method	Méthode milligrammique Milligram method	$x \times 10^{-3}$	$x \times 10^{-1}$	1 : 10^{3}
Ultramicrométhode Ultramicro method	Méthode microgrammique Microgram method	$x \times 10^{-4}$—$x \times 10^{-6}$	$x \times 10^{-2}$—$x \times 10^{-5}$	1 : 10^{5}
Submicro ou ultra-ultramicrométhode Submicro or ultra-ultramicro method	Méthode nanogrammique Nanogram method	$x \times 10^{-7}$—$x \times 10^{-9}$	$x \times 10^{-6}$—$x \times 10^{-8}$	1 : 10^{9}
Submicrométhode Subultramicro method	Méthode picogrammique Picogram method	$x \times 10^{-10}$—$x \times 10^{-12}$	$x \times 10^{-9}$	1 : 10^{12}

x = nombre compris entre 1 et 10. x = any number from 1 to 10.

SECTION OF ANALYTICAL CHEMISTRY

COMMISSION ON MICROCHEMICAL TECHNIQUES*

RECOMMENDATIONS FOR TERMINOLOGY TO BE USED WITH PRECISION BALANCES

EMPFEHLUNGEN ZUR TERMINOLOGIE BEI PRÄZISIONSWAAGEN

RECOMMANDATIONS SUR LA TERMINOLOGIE CONCERNANT LES BALANCES DE PRÉCISION

Load shall be the total weight acting, after counterbalancing, upon the terminal bearing which carries the object of weighing.

Belastung sei das Gesamtgewicht, das nach erfolgtem Austarieren auf jene Endschneide wirkt, die das Objekt der Wägung trägt.

Charge est le poids total agissant, après tarage, sur le couteau qui porte l'objet à peser.

Capacity shall be the maximum safe load claimed by the manufacturer.

Tragfähigkeit sei die vom Hersteller vorgesehene Höchstbelastung.

Capacité, charge maximum indiquée par le constructeur.

Precision of indication shall be the standard deviation of the instrument indication, i, for a stated load.

Präzision der Anzeige sei die mittlere Schwankung der Instrumentanzeige, i, für eine angegebene Belastung.

Précision de lecture (indication) est la déviation standard des indications, i, de la balance pour une charge donnée.

Value of division (in weight units per division of the pointer scale) is determined by empirical calibration. It is the reciprocal of the sensitivity and, like the latter, usually varies somewhat with the load.

* M. K. Zacherl (Austria), H. Malissa (Germany), A. A. Benedetti-Pichler (U.S.A.), E. Abrahamczik (Germany), R. Belcher (U.K.), C. L. Wilson (U.K.), H. Lieb (Austria), P. E. Wenger (Switzerland), P. H. Kirk (U.S.A.).

Wert des Teilstriches (in Gewichtseinheiten pro Teilstrich der Zeigerskala) wird durch empirische Eichung bestimmt. Er ist der Empfindlichkeit reziprok und ändert sich wie diese in der Regel etwas mit der Belastung.

Valeur d'une division (en unités de poids par division de l'échelle) est déterminée empiriquement. C'est l'inverse de la sensibilité et comme celle-ci varie en général un peu avec la charge.

Instrument indication, i, is the observed deflection or rest point multiplied by the value of the division for the load in question.

Instrumentanzeige, i, ist der beobachtete Ausschlag oder Ruhepunkt multipliziert mit dem Wert des Teilstriches für die betreffende Belastung.

Indication de l'instrument, i, pour une charge déterminée est le produit de la valeur d'une division par le nombre de celles-ci (indiqué par l'aiguille ou l'index de la balance).

No-load indication, i_0, is the deflection or rest point (no-load reading), multiplied by the value of the division for zero load (rider at zero).

Leeranzeige, i_0, sei der Ausschlag oder Ruhepunkt (Leerablesung) der unbelasteten Waage multipliziert mit dem Wert des Teilstriches für Last Null (Reiter auf Null).

Indication (valeur) à vide, i_0, est le produit de la valeur d'une division par le nombre de celles-ci, indiqué par l'index (aiguille) lorsque la balance n'est pas chargée.

Deflection (in divisions of the pointer scale) is the other point of reversal of an ideal swing starting at the zero point of the pointer scale. Since the points of reversal of an ideal swing are located symmetrically around the rest point, the deflection is equal to twice the rest point.

Ausschlag (in Teilstrichen der Zeigerskala) entspricht dem zweiten Umkehrpunkt einer ungedämpften Schwingung des Zeigers, die am Nullpunkt der Zeigerskala beginnt. Da eine ungedämpfte Schwingung symmetrisch um den Ruhepunkt erfolgt, ist der Ausschlag das Doppelte des Ruhepunktes.

Déflexion (exprimée en divisions de l'échelle) est donnée par la seconde position de retour de l'aiguille dans les cas d'oscillations non amorties, lorsque le départ de celle-ci a lieu au point 0 de l'échelle. Comme une oscillation non amortie se fait symétriquement par rapport à la position de repos, la déviation correspond au double de cette position.

Rest point is the position of the pointer with respect to the pointer scale when the motion of the beam has ceased.

Ruhepunkt ist die Zeigerstellung mit ruhendem Balken.

Position de repos est la position de l'aiguille par rapport à la graduation lorsque les oscillations du fléau ont cessé.

Zero point of scale indicates the rest point of the properly adjusted balance with no load on the pans and the rider (chain) in zero position.

Nullpunkt der Zeigerskala gibt den Ruhepunkt der unbelasteten und richtig eingestellten Waage mit Reiter (Kettengewicht *etc.*) in Nullstellung.

Zéro de l'échelle correspond à la position de repos de la balance non chargée et correctement ajustée, le cavalier étant placé sur le zéro de l'échelle du fléau.

Sensitivity for a stated load shall be the response per unit of mass in divisions of the pointer scale per unit of mass.

Empfindlichkeit für eine angegebene Belastung sei das Verhältnis der Änderung der Zeigerablesung zur Grösse der sie verursachenden Gewichtsänderung (Teilstriche per Gewichtseinheit).

Sensibilité, pour une charge donnée, sera l'effet de l'unité de masse exprimé en divisions de l'échelle par unité de masse (nombre de traits de la graduation par unité de masse (poids)).

Readability shall be the smallest fraction of a division to which the index scale can be read with ease either by estimation or by use of a vernier. It should normally be expressed in divisions of the pointer scale.

Ablesbarkeit sei der kleinste Bruchteil eines Teilstriches, der noch leicht entweder durch Schätzung oder unter Benutzung eines Nonius—wenn ein solcher gegeben ist—bestimmt werden kann. Als Einheit diene der Teilstrich der Zeigerskala.

Appréciation de la lecture est la plus petite fraction d'une division susceptible d'être appréciée, soit par lecture directe, soit à l'aide d'un vernier.

Milligram equivalent of readability shall be the product of readability and value of the scale division (in milligrams per division).

Milligrammäquivalent der Ablesbarkeit sei das Produkt aus Ablesbarkeit und Wert des Teilstriches in Milligramm per Teilstrich.

Sensibilité de la lecture en milligrammes équivalents est le produit de l'appréciation par la valeur en milligrammes correspondant à une division de l'échelle.

APPLICATIONS ANWENDUNGEN APPLICATIONS

Precision of a balance shall be stated as standard deviation of the instrument indication for a stated load (l_{20}, for 20 g). A statement of the procedure, conditions, and experience of observer should be included.

Genauigkeit der Waage sei die mittlere Schwankung der Anzeige für eine angegebene Belastung (l_{20}, für 20 g). Angaben über Wägeverfahren, Arbeitsbedingungen und Erfahrung des Beobachters sollen beigefügt werden.

Précision de la balance est la déviation standard des indications de l'instrument pour une charge donnée (l_{20}, tare 20 g). Des précisions doivent être données sur les conditions de pesée et sur l'habileté expérimentale de l'observateur.

Range of applicability of balance as function of capacity and precision

Anwendungsbereich der Waage in Abhängigkeit von Tragfähigkeit und Präzision

Limite d'application de la balance en ce qui concerne la capacité et la précision

Balance Waage Balance	*Capacity in Tragfähigkeit in Capacité en* g	l_{mg}
Analytical balance Analysenwaage Balance analytique	50–200	0·01–0·05
Microchemical balance Mikrochemische Waage Balance microchimique	5–20	0·001–0·005
Assay balance Probierwaage Balance d'essai	1–5	0·0005–0·002

Precision of a weighing depends upon the method of weighing and upon the precision of indication, l, for the load in question.

Präzision der Wägung hängt vom Wägeverfahren und der Präzision der Anzeige, l, bei der betreffenden Belastung ab.

Précision de la pesée dépend de la méthode de pesée et de la précision de l'indication, l, pour la charge en question.

Methods Wägeverfahren Méthodes	*Precision Präzision Précision*
Direct weighing Proportionalwägung Pesée directe	$\pm (l^2 + l_0^2)^{\frac{1}{2}}$
For small loads Bei kleinen Belastungen Pour faible charge	$1{\cdot}4\ l_0$
Substitution Substitutionswägung Substitution	$1{\cdot}4\ l$
Transposition Gauss'sche Doppelwägung Transposition	$l/1{\cdot}4$

Correction of direct weighings—Direct weighings are corrected by subtracting the no-load indication. Direct weighings to be used for the determination of the arm ratio must be corrected for the no-load indication.

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Berichtigung von Proportionalwägungen—Subtrahieren der Leeranzeige berichtigt Proportionalwägungen für Abweichungen der Leeranzeige von Null. Proportionalwägungen, die für die Bestimmung des Armverhältnisses benutzt werden sollen, müssen für die Leeranzeige berichtigt werden.

Correction de la pesée directe—La pesée directe est corrigée par soustraction de l'indication de la balance à vide. La pesée directe, utilisée pour la détermination du rapport des bras de levier doit être corrigée en tenant compte de l'indication de la balance non chargée.

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SECTION OF ANALYTICAL CHEMISTRY

PRELIMINARY RECOMMENDATIONS ON NOMENCLATURE AND PRESENTATION OF DATA IN GAS CHROMATOGRAPHY*

Following approaches made to the International Union of Pure and Applied Chemistry by Dr F. H. Stross and Dr D. Ambrose, a special group was formed under the auspices of the Section of Analytical Chemistry to make recommendations for a standard terminology in gas chromatography. The Group consisted of Dr D. Ambrose, Chairman (U.K.), Dr A. T. James (U.K.), Professor A. I. M. Keulemans (The Netherlands), Dr E. Kováts (Switzerland), Dr H. Röck (Germany), Dr C. Rouit (France) and Dr F. H. Stross (U.S.A.).

The Group adopted the following objectives:

(1) To recognize and encourage existing, well established conventions, to the extent that they are basically sound (consistent with accepted theory) and of general utility.

(2) To endeavour to suppress confusion by selecting a single term from the multiplicity that, in some cases, have been proposed to describe or measure a particular concept in gas chromatography. This is considered necessary regardless of how theoretically sound the various duplicating terms may be. Two or more terms for a single property should only be recognized when each of the terms has a specific area where its use is clearly of great advantage.

(3) To attempt to eliminate ambiguity by altering definitions or usages that are vague or inconsistent with the Recommendations.

(4) To make these Recommendations so clear and concise that they will find universal acceptance and utilization to the greatest possible extent.

The work of the Group has been conducted by correspondence and has resulted in the recommendations which follow; before being drawn up in their final forms they were shown to a large number of those interested in the subject and modifications were introduced in the light of comments received by the Chairman. In particular we must acknowledge the contribution made by the Groupement pour l'Avancement des Méthodes Spectrographiques who had independently been considering the same subject under the chairmanship of Professor P. Chovin. In submitting our recommendations

* Comments and suggestions should be sent to Dr D. Ambrose, National Chemical Laboratory, Teddington, Middlesex, England.

for wider consideration we express our hope that they will serve the purposes we have defined above and that, now a start has been made, it will be possible to revise them and keep them up to date as their inadequacies are revealed.

Signed: D. AMBROSE, A. T. JAMES, A. I. M. KEULEMANS, E. KOVÁTS, H. RÖCK, C. ROUIT, F. H. STROSS.

July, 1959

1. INTRODUCTION

Gas Chromatography is so widely used that it has become necessary to standardize definitions and presentation of results. Recommendations having this objective should be in harmony with gas chromatographic theory and account has been taken of this in the following proposals.

Gas chromatography is almost always carried out by elution. The recommendations pertaining to the presentation of results and general background (item **5** and following) are restricted to elution, mainly gas–liquid, chromatography; further recommendations will be required for gas–solid chromatography. The definitions of terms (items **2** to **4**) are nearly all generally applicable without restriction.

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2. NAME OF TECHNIQUE

Gas chromatography comprises all chromatographic methods in which the moving phase is a gas (the word chromatography itself implies that a stationary phase is present in addition to the moving phase).

Gas–liquid chromatography comprises all gas chromatographic methods in which the stationary phase is a liquid distributed on a solid support. Separation is achieved by partition of the components of a sample between the phases.

Gas–solid chromatography comprises all gas chromatographic methods in which the stationary phase is an active solid (e.g. charcoal, molecular sieves). Separation is achieved by adsorption of the components of a sample.

3. APPARATUS

Sample injector

A sample injector is a device by which a liquid or gaseous sample is introduced into the apparatus. The sample can be introduced directly into the carrier gas stream, or into a chamber temporarily isolated from the system by valves which can be changed so as to make an instantaneous switch of the gas stream through the chamber. The latter is a *by-pass injector*.

Column

Solid volume is the volume occupied by the solid support or the active solid in the column.

Liquid volume V_L is the volume occupied by the liquid phase in the column. $V_L = w_L/\rho_L$, where w_L is the weight of the liquid in the column, and ρ_L is its density at the column temperature.

Interstitial volume is the volume of the column not occupied by the liquid phase and its solid support, or by the active solid. It does not include any volume external to the column, such as the volume of the sample injector or of the detector.

Detector

A detector is a device that measures the change of composition of the effluent. A detector that measures instantaneous concentration is called a *differential detector*. An *integral detector* continuously measures the sample accumulated from the beginning of the analysis.

4. REAGENTS

Carrier gas or eluent gas is gas that is used to elute the sample as it passes through the column. The carrier gas forms the *mobile phase*.

Liquid phase is a liquid which is relatively non-volatile at the column temperature and is sorbed on the solid support, where it acts as a solvent for the sample. Separation depends on differences in solubility of the various components of the sample in the liquid phase.

Solid support is normally an inert porous solid, which sorbs the liquid phase. The particle-size range of the support affects column efficiency and the pressure differential necessary to achieve a given flow rate. Modifications of the method have been introduced for the achievement of special separations, in which the solid support is not inert but is an active solid. In capillary columns the inner wall of the column serves as the solid support and obviates the use of additional porous solids for this purpose.

Active solid is a porous solid with adsorptive properties by means of which chromatographic separations may be achieved. The separations resulting from this action follow laws different from those deriving from the partitioning action of the liquid phase.

In gas–liquid chromatography the *stationary phase* comprises the liquid phase without the solid support. In gas–solid chromatography the *stationary phase* is the active solid.

5. CHROMATOGRAM RECORDS

A *chromatogram* is a plot of the detector response *versus* time or volume of carrier gas. Idealized chromatograms obtained with differential and integral detectors for one component are shown in *Figure 1*.

The definitions in this paragraph apply to the chromatograms obtained directly by means of differential detectors or by differentiating the records obtained by means of integral detectors. The *base line* is that portion of a chromatogram recorded when only carrier gas emerges from the column. A *peak* is the portion of the chromatogram recording the detector response while a single component emerges from the column (if separation of a mixed sample is incomplete, two or more components may appear as one peak). The *peak base* CD is an interpolation of the base line between the extremities of the peak. The area enclosed between the peak and the peak base is the *peak area* and the distance BE from the peak maximum to the peak base measured parallel to the axis representing detector response is the *peak height*. The segment of peak base FG intercepted by tangents to

the inflection points on either side of the peak is the *peak width*. The line parallel to the peak base, bisecting the peak height, and terminating at the sides of the peak HJ is the *peak width at half height*.

The following definitions apply to chromatograms obtained with integral detectors. As a sample component passes through the detector, a sigmoid curve is obtained and the base line is displaced to a new position. The change in base line position caused by the sample component is known as a *step*, and the difference in the heights of the two base lines is the *step height*.

6. RETENTION PARAMETERS

Retention volume (uncorrected), V_R is the volume of gas required to elute the compound under study, and is given by

$$V_R = t_R F_e \qquad (1)$$

where t_R is the *retention time*, the time for the emergence of the peak maximum after injection of the sample, and F_e is the volumetric flow rate of the carrier gas measured at the outlet pressure and the temperature of the column. V_R, t_R correspond to OB in *Figure 1* which, in the remaining definitions, is assumed to have the carrier gas volume as horizontal axis.

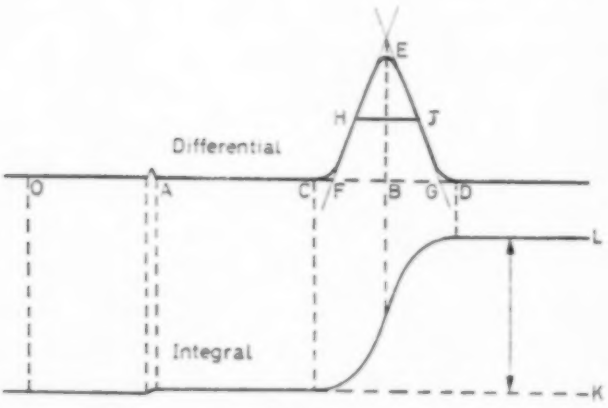

Figure 1

Gas hold-up, V_M is the uncorrected retention volume of a non-absorbed sample and is the volume of carrier gas required to transport such a sample from the point of injection to the point of detection at column outlet pressure. It includes contributions due to the interstitial volume of the column, and the effective volumes of the sample injector and the detector. It can readily be determined for any column by elution of some material for which the partition coefficient is very small compared with its value for other solutes. Gases such as nitrogen, air or the noble gases are normally employed for this purpose. The peak often produced by the presence of small amounts of air during the sample injection gives this information, and is referred to as the *air peak*.

For a capillary column the interstitial volume may be calculated from the dimensions. The interstitial volume divided by j (see below) is the contribution to V_M due to the column and the contribution due to the apparatus may therefore be determined.

Adjusted retention volume, V'_R is given by

$$V'_R = V_R - V_M = AB \tag{2}$$

Corrected retention volume, V°_R is given by

$$V^\circ_R = jV_R = j(OB) \tag{3}$$

This quantity is of limited use because it is influenced by the volumes of sample injector and detector as well as the interstitial volume of the column. The symbol j in equation (3) is the *pressure gradient correction factor* for a homogeneously filled column of constant diameter and is given by

$$j = \frac{3}{2}\left\{\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1}\right\} \tag{4}$$

where p_i, p_0 are the pressures of the carrier gas at the inlet and the outlet of the column respectively. Use of the factor j allows for the fact that in gas chromatography the mobile phase is compressible. If in fact the flow rate is measured at the inlet of the column, the corrected retention volume may be obtained by using a suitably modified expression for j.

Net retention volume, V_N is given by

$$V_N = jV'_R = j(AB) \tag{5}$$

Specific retention volume, V_g is the net retention volume at 0°C per gram of liquid phase and is given by

$$\frac{V_N}{w_L} = \frac{V_g T}{273} \tag{6}$$

where T is the absolute temperature of the column. V_N/w_L is the net retention volume per gram at the column temperature.

Retention volumes may be expressed relative to the retention volume of a standard component on the same column at the same temperature. *Relative retention*, r is given by

$$r_{12} = \frac{V_{g1}}{V_{g2}} = \frac{V_{N1}}{V_{N2}} = \frac{V'_{R1}}{V'_{R2}} \neq \frac{V_{R1}}{V_{R2}} \tag{7}$$

where the subscripts refer to components 1 and 2. Component 2 is the standard. Relative retentions measured from the point of injection can only be considered independent of column dimensions if $V_M \ll V_{R1}$, V_{R2}. When, as is usual and desirable, relative retentions are determined from one chromatogram in which experimental conditions are constant and identical for both components, the determination is simplified to the measurement of the appropriate distances on the recorder chart (*i.e.* the distances corresponding to the adjusted retention volumes).

Partition coefficient, K is defined as

$$K = \frac{\text{(weight of solute)/(ml stationary phase)}}{\text{(weight of solute)/(ml mobile phase)}}$$

and is assumed to be independent of concentration at the concentrations prevailing in gas chromatography.

According to elementary theory, which has been adequately verified by experiment, the partition coefficient is related to the retention volume by

$$K = \frac{V_N}{V_L} = \frac{V_N \rho_L}{w_L} = \frac{V_g T \rho_L}{273} \tag{3}$$

The specific retention volume, the relative retention and the partition coefficient are independent of column parameters but they do depend upon the samples involved, the partitioning system and the temperature.

Meaning of qualifying signs—In definitions of retention parameters the superscript ° indicates that the pressure correction factor has been applied, and the prime ′ that measurements are made from the air peak. However, the symbol for net retention volume in accordance with this scheme is unduly cumbersome, and V_N has been substituted for it.

7. RECOMMENDATIONS: RETENTION DATA

Measurements of retention data should be reported in such a manner that they can be converted for use in experiments with other apparatus and under different conditions. This can be done on an absolute basis, by measurement of the partition coefficient or specific retention volume; or on a relative basis, by measurement of relative retentions, relative to a standard solute. For determining the relative retentions of a series of substances a standard should be chosen such that its retention volume falls near the middle of the series. Standards with very small retention volumes should not be used. The following substances are suggested as suitable standards for medium temperature work (*i.e.* up to 150°C):

n-butane
2,2,4-trimethylpentane (iso-octane)
benzene
p-xylene
naphthalene
methylethylketone
cyclohexanone
cyclohexanol

All these substances can be obtained easily in adequate purity and they cover a wide range of retention volumes, but if none of them is suitable for a particular problem some other easily available laboratory chemical should be used.

Temperature effects

Whenever possible the variation of retention volume with temperature should be found and results reported for at least two temperatures, as far apart as is practicable. If results are sufficiently extensive, a suitable graphical method is a plot of the logarithm of the relative retention against the reciprocal of the absolute temperature. Variation of specific retention volume may be expressed in a similar way or by means of an Antoine equation:

$$\log V_g = A + \frac{B}{t + C} \tag{9}$$

in which t is the column temperature in °C and A, B, C are constants. The relations so obtained can conveniently be used for interpolation.

Experimental details

The following experimental variables should be published with any set of results laying claim to being quantitative in nature:

nature and particle-size range of solid support;
nature, concentration and amount of liquid phase in the column;
sample size;
column dimensions (length and internal diameter);
column inlet and outlet pressures;
flow rate of carrier gas and method of measurement;
temperature of column and accuracy of temperature control;
description of detector, *e.g.* type of sensing element, cell geometry, cell volume, response time.

8. APPARATUS PERFORMANCE

Column performance—An expression of column performance in terms of theoretical plate number n can be calculated by the equation

$$n = 16 \times \left(\frac{\text{retention volume}}{\text{peak width}}\right)^2 = 16\left(\frac{OB}{FG}\right)^2 \tag{10}$$

(see *Figure 1*). The theoretical plate number may vary with the compound as well as the column. Therefore the compound used should be specified. The units for retention and peak width used in equation (10) must be consistent so that their ratio n is dimensionless. If the corrected retention volume is used, the observed peak width must also be corrected for pressure drop in the column.

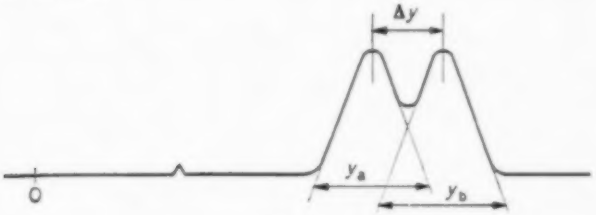

Figure 2

Peak resolution—If two compounds are well enough separated to permit a satisfactory estimation of the peak width, and the peaks are approximately Gaussian, as shown in *Figure 2*, the resolution may be expressed by

$$\text{Resolution} = 2 \times \frac{\text{difference between retention volumes}}{\text{sum of peak widths}} \qquad (11)$$

$$= 2\Delta y/(y_a + y_b)$$

By relating equations (7), (10) and (11), it is then possible to calculate the number of plates required for a specified resolution.

$$n = \left\{2 \times \text{Resolution} \frac{(r+1)}{(r-1)}\right\}^2 \qquad (12)$$

9. DISCUSSION

The partition coefficient for a given solute–solvent system is (for conditions prevailing in gas–liquid chromatography) a physical constant dependent only on the temperature, and gas–liquid chromatography provides a convenient method for its determination. The specific retention volume V_g has the same character of a general constant, and can easily be converted to K by relation (8). In the determination of K it is necessary to determine the density of the solvent at the column temperature (to about 1 per cent) while this is not necessary for the determination of V_g. The other column variables and operating conditions, however, have to be accurately known since they enter into the computation of K and V_g, as can be seen from the relations given above.

In the determination of relative retentions, it is not necessary to know any column variables (*e.g.* F_c, w, p_1, p_0), except the temperature; all that is necessary is that they remain constant. Furthermore, relative retentions do not vary with temperature as much as do absolute measurements and they are therefore to be preferred unless the variables listed can be determined with accuracy. Relative retentions, used with standard substances as suggested above, are immediately useful for the identification of compounds if tables of retentions including the compounds in question are available.

It is important to specify the ratio of liquid phase to solid support precisely. The activity of the latter can be such as to influence appreciably the chromatographic separations achieved; this effect will be more pronounced the lower the amount of liquid phase covering the solid.

Errors

The following factors can affect the retention parameters and will cause errors unless they are corrected for: sample size, method of injection and detector dead volume. These factors affect not only the retention parameters but also the peak shape, and therefore can give misleading results also in the calculation of efficiency and resolution. These calculations, then, should not be relied on unless the distorting factors are small, and the peaks obtained nearly Gaussian.

Experimental considerations

The flow rate F_c is required at the temperature and outlet pressure of the column, whereas measurements of flow are usually made at room temperature. Suitable corrections must therefore be made: if a capillary flowmeter is used, the pressure drop across the meter must be considered; with wet flowmeters allowance must be made for the vapour pressure of water. If F is the flow rate of the saturated gas determined from the flowmeter at pressure p, and p_w is the vapour pressure of water at the temperature of the flowmeter, the partial pressure of the carrier gas, p_M is given by

$$p_M = p - p_w$$

and

$$F_c = F(p - p_w)/p \qquad (13)$$

The carrier gas should enter the column at column temperature; the sample should be made to vaporize very rapidly on injection in order to avoid artifacts of efficiency or resolution.

In absolute measurements, account must be taken of the temperature of operation in assessing the life of the column before a significant change in w_L occurs. The rate of variation of the partition coefficient with temperature is similar in magnitude to that of vapour pressure, and the accuracy of temperature control, both with time and along the column, needs to be specified.

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TABLE OF TERMS

English	*French*	*German*	
Gas chromatography	Chromatographie des gaz	Gas-Chromatographie	
Gas-liquid chromatography	Chromatographie gaz-liquide	Gas-Flüssigkeit-Chromatographie	
Gas-solid chromatography	Chromatographie gaz-solide	Gas-Festkörper-Chromatographie	
Sample injector	Injecteur d'échantillon	Probeninjektor	
By-pass injector	Injecteur à dérivation	Umleitinjektor	
Differential detector	Détecteur différentiel	Differentialdetektor	
Integral detector	Détecteur intégral	Integraldetektor	
Solid volume	Volume solide	Festkörpervolumen	
Liquid volume	Volume liquide	Flüssigkeitsvolumen	
Interstitial volume	Volume interstitiel	Gasraumvolumen	
Carrier gas	Gaz porteur	Trägergas	
Mobile phase	Phase mobile	mobile Phase	
Stationary phase	Phase stationnaire	stationäre Phase	
Liquid phase	Phase liquide	flüssige Phase	
Solid support	Support solide	inaktiver *oder* aktiver fester Träger	
Active solid	Solide actif	Adsorbens	
Chromatogram	Chromatogramme	Chromatogramm	
Base line	Ligne de base	Basislinie	
Peak	Pic	Pik*	
Peak base	Base du pic	Pikbasis	
Peak area	Surface du pic	Pikoberfläche	
Peak height	Hauteur du pic	Pikhöhe	
Peak width	Largeur du pic	Pikbreite	
Peak width at half height	Largeur du pic à demi-hauteur	Pikbreite bei halber Höhe	
Step	Palier	Stufe (in einem Integral-Chromatogramm)	
Step height	Hauteur de palier	Stufenhöhe (in einem Integral-Chromatogramm)	
Retention volume	Volume de rétention	unkorrigiertes Retentionsvolumen	V_R
Adjusted retention volume	Volume de rétention réduit	reduziertes Retentionsvolumen	V'_R
Corrected retention volume	Volume de rétention limite	korrigiertes Retentionsvolumen	V^0_R
Net retention volume	Volume de rétention absolu	Netto-Retentionsvolumen	V_N
Specific retention volume	Volume de rétention spécifique	spezifisches Retentionsvolumen	V_g
Pressure gradient correction factor	Facteur de correction du gradient de pression	Korrekturfaktor für den Druckgradienten	j
Gas hold-up	Retenue de gaz	Nullretentionsvolumen	V_M
Relative retention	Rétention relative	relative Retention	r_{12}
Partition coefficient	Coefficient de partage	Verteilungskoeffizient	K
Column performance	Efficacité de la colonne	Trennschärfe der Kolonne	
Peak resolution	Résolution des pics	Pikauflösung	
Number of theoretical plates	Nombre de plateaux théoriques	Zahl der theoretischen Stufen der Kolonne	n

* In der deutschsprachigen Fachliteratur wird sehr oft das Wort "peak" als solches gebraucht. In der Umgangssprache wird das gleiche Wort so oft verwendet, dass die Autoren sich entschlossen, das Wort in obenstehender Schreibweise vorzuschlagen, umsomehr als es früher in der deutschen Sprache gebraucht wurde (vgl: *Der Grosse Duden*, Bibliographisches Institut AG, Leipzig, 1932: der Pik, des Pikx, die Pike).

DISSOCIATION CONSTANTS OF ORGANIC ACIDS IN AQUEOUS SOLUTION

DISSOZIATIONSKONSTANTEN ORGANISCHER SÄUREN IN WÄSSERIGER LÖSUNG

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COMMISSION ON ELECTROCHEMICAL DATA*

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ABTEILUNG FÜR ANALYTISCHE CHEMIE

KOMMISSION FÜR ELEKTROCHEMISCHE DATEN*

DISSOZIATIONSKONSTANTEN ORGANISCHER SÄUREN IN WÄSSERIGER LÖSUNG

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INTRODUCTION

The present Tables of dissociation constants of organic acids in aqueous solutions have been prepared at the request, and with the assistance, of the International Union of Pure and Applied Chemistry (I.U.P.A.C.). The Tables form a part of the work of the Commission on Electrochemical Data, whose task has been to collect reliable data of general interest, and especially of analytical interest, in order to make such data more readily accessible for practical and theoretical applications. It has therefore been necessary not only to cover the information given in the literature as completely as possible, but also to evaluate it critically; the user of the Tables should therefore be in a position to choose the most reliable figure even though several contradictory values may have been given.

Two aspects have to be taken into account in assessing the reliability of the values.

(1) *The experimental variables*—These include the nature of the system under study, the reproducibility of the measurements, the purity and stability of the materials being investigated (e.g. isomeric content) and of the solvents used, the constancy of the temperature, etc. Inevitably, it has not always been possible to evaluate these variables, and in most cases the effect of possible impurities or the presence of small concentrations of isomers cannot be estimated, especially if the properties of these isomers differ only slightly. Nevertheless, we have attempted to reach a conclusion as to the reliability of the measurements from the general character of the work done.

(2) *The method of measurement and the procedure for evaluating the quality of the measurement*—Under this heading are considered all the parameters inherent in the method of measurement, the range of concentrations used, the graphical or mathematical methods involved in the extrapolation of the results to zero ionic strength, and the various relations required for the evaluation, which may be theoretical or wholly or partly empirical.

Despite such a critical approach, it has not always proved possible to reach a conclusion in every case as to which of the several values of a constant is the most reliable. In particular, exact information on the probable error in the measurements is only rarely obtainable. We have therefore limited ourselves to a qualitative assessment, and a number of ranges of uncertainty are designated as "very reliable" (s.zuv.), with an estimated uncertainty of some tenths of a per cent ($\Delta pK \simeq \pm 0{\cdot}0005$); "reliable" (zuv.), with an estimated uncertainty of ~ 1 per cent ($\Delta pK \simeq \pm 0{\cdot}005$); "approximate" (rel.zuv.), with an estimated uncertainty of several per cent ($\Delta pK \leq \pm 0{\cdot}04$); "uncertain" (uns.), with an estimated uncertainty of more than 10 per cent ($\Delta pK > \pm 0{\cdot}04$).

This does not mean that, for example, a value designated as "uncertain" cannot agree with a "reliable" value. The designation "uncertain" simply signifies that the value given may be in error by over 10 per cent

EINFÜHRUNG

Die vorliegenden Tabellen der Dissoziationskonstanten von Säuren in wässeriger Lösung wurden im Auftrag und mit Unterstützung der "International Union of Pure and Applied Chemistry" (I.U.P.A.C.) aufgestellt, und zwar im Rahmen der Aufgabe, die der Kommission für elektrochemische Daten gestellt war, zuverlässige elektrochemische Daten von allgemeinem und speziell auch analytischem Interesse zu sammeln und dadurch einem größeren Kreis zur praktischen und theoretischen Benützung zugänglich zu machen. Wir haben unsere Aufgabe deshalb darin gesehen, nicht nur die vorhandenen Literaturangaben möglichst lückenlos zusammenzustellen, sondern diese Angaben auch kritisch zu werten, damit der Benutzer der Tabellen in der Lage ist, aus den oft zahlreichen und einander widersprechenden Werten die zuverlässigsten auszuwählen.

Für die Beurteilung der Zuverlässigkeit der angegebenen Werte sind im wesentlichen zwei Punkte zu prüfen.

(1) *Die experimentellen Voraussetzungen*—Hierher gehören die verwendete Meßanordnung, die angegebene Reproduzierbarkeit der Messungen, Angaben über die Reinheit und Beständigkeit der untersuchten Stoffe (z.B. Gehalt an Isomeren) und des Lösungsmittels, die Temperaturkonstanz usw. Eine sichere Beurteilung dieser Voraussetzungen ist allerdings nicht immer zu erreichen. So ist es z.B. in den meisten Fällen nicht möglich, den Einfluß evtl. noch vorhandener Verunreinigungen oder der Anwesenheit geringer Mengen von Isomeren abzuschätzen, insbesondere dann, wenn die Konstanten dieser Isomeren sich nicht wesentlich unterscheiden. Immerhin haben wir versucht, auch aus dem Gesamtcharakter einer Arbeit auf die Zuverlässigkeit der Meßwerte zu schließen.

(2) *Die verwendete Meßmethode und das zur Auswertung der Messungen benutzte Verfahren*—Hierher gehören alle im Meßverfahren steckenden Voraussetzungen, die zur Extrapolation der Meßwerte auf verschwindende interionische Wechselwirkung benutzten graphischen oder rechnerischen Methoden, der verwendete Konzentrationsbereich der Messung, die zur Auswertung herangezogenen theoretischen Gesetze und halb- oder ganzempirischen Regeln.

Trotz einer solchen kritischen Analyse ist es nicht immer möglich, in jedem Einzelfall zu einer gesicherten Aussage zu gelangen, welcher von mehreren vorliegenden Werten der sicherste ist. Insbesondere sind quantitative Angaben über den wahrscheinlichen Fehler der Meßergebnisse nur sehr selten möglich. Wir beschränken uns deshalb auf qualitative Angaben und bezeichnen die angegebenen Zahlenwerte als "sehr zuverlässig" (s.zuv.) bei einer geschätzten Unsicherheit von einigen Zehntel Prozent ($\Delta pK \simeq \pm 0{,}0005$); "zuverlässig" (zuv.) bei einer geschätzten Unsicherheit von ~ 1 Prozent ($\Delta pK \simeq \pm 0{,}005$); "relativ zuverlässig" (rel.zuv.) bei einer geschätzten Unsicherheit von einigen Prozent ($\Delta pK \leqslant \pm 0{,}04$); "unsicher"

because of the experimental conditions (which are not always stated), the method used, or the extrapolation procedure (which is often not considered); any agreement, therefore, between "reliable" and "uncertain" values must be regarded as fortuitous. Values of K which are extremely small or large must normally be regarded as basically uncertain, because of the difficulties in determining them accurately. The classification of the published constants has naturally been to some extent a subjective process, having been based on so many considerations that absolute validity can scarcely be claimed; however, we have endeavoured to carry out this qualitative evaluation of the data as impartially as possible. If there are contradictions between the present assessment and the accuracy claimed by the authors in the original work, the reasons are stated briefly so that the reader can form his own judgement with the aid of the original literature.

A critical study of this type naturally demands a complete survey of the original literature. The dissociation constants are, as far as possible, the thermodynamic K values relating to zero ionic strength*, $I=0$. The classical constants K_c or K_m appear in the Tables only when other values are not available. For this reason only the literature from 1927 (up to and including 1956) has been considered, and earlier results have been included only in exceptional cases where it was possible to extrapolate them to $I=0$. The earlier K_c values are collected in the *Landolt-Börnstein Tables* and in the *International Critical Tables*. We have also limited ourselves to pure aqueous solutions, for the constants in other solvents are of less general interest and are always rather uncertain. All work relating to the measurement of constants in partially aqueous media, e.g. in aqueous solutions to which a solvent such as ethanol has been added to increase the solubility, has therefore been ignored. It is planned to publish further tables for bases in aqueous solutions.

The Tables proper are preceded by several introductory parts. In Part I, the different techniques for measurement are critically discussed; reference to this part can therefore be made in each case. Part II contains an explanation of the symbols used in the Tables. Part III indicates the sequence in which the various types of acid are dealt with. Part IV consists of the Tables themselves, and the relevant references to the literature are listed in Part V.

Note: The Tables are published in German only, but appropriate reference to the English versions of the Index and of Parts I, II and III should suffice to prevent confusion even when the reader is not fully conversant with German.

* The symbol J is used for ionic strength in the German version and in the Tables.

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(uns.) bei einer geschätzten Unsicherheit von mehr als 10 Prozent ($\Delta pK > \pm 0{,}04$).

Das bedeutet nicht, daß z.B. ein als "unsicher" bezeichneter Wert nicht mit einem "zuverlässigen" Wert übereinstimmen könnte. Die Bezeichnung "unsicher" besagt dann nur, daß auf Grund der angegebenen (oder fehlenden) Meßbedingungen oder der verwendeten Methode oder des benutzten (oder nicht berücksichtigten) Extrapolationsverfahrens der Meßwert von dem angegebenen um mehr als 10 Prozent hätte abweichen können, daß also die Übereinstimmung mit einem anderen zuverlässigen Wert als zufällig angesehen werden muß. K-Werte, die extrem klein oder groß sind, müssen prinzipiell als unsicher betrachtet werden, da sie mit exakten Methoden nicht erfaßt werden können. Insgesamt kann natürlich eine auf der Berücksichtigung so zahlreicher Faktoren beruhende und auch subjektiver Beurteilung unterliegende Einordnung der Meßwerte keinen Anspruch auf absolute Gültigkeit erheben, wir haben uns jedoch bemüht, diese qualitative Bewertung der angegebenen Daten so vorurteilslos wie möglich durchzuführen. Soweit Widersprüche in der Beurteilung der Meßwerte mit Genauigkeitsangaben der Autoren der Originalarbeiten vorliegen, werden die Gründe dafür stichwortartig angegeben, so daß der interessierte Leser sich an Hand der Originalliteratur darüber ein eigenes Urteil bilden kann.

Eine derartige kritische Wertung der Meßergebnisse verlangte natürlich, daß die Werte aus der Originalliteratur selbst entnommen wurden. Die angegebenen Dissoziationskonstanten sind, soweit möglich, thermodynamische, auf die Ionenstärke $\mathcal{J}=0$ extrapolierte K-Werte. Nur wenn solche fehlten, wurden auch klassische Konstanten K_c bzw. K_m in die Tabelle aufgenommen. Aus diesem Grund wurde nur die Literatur von 1927 bis incl. 1956 berücksichtigt, ältere Arbeiten nur in Ausnahmefällen, wenn auf $\mathcal{J}=0$ extrapoliert werden konnte. Die älteren K_c-Werte sind in den *Landolt-Börnstein-Tabellen* bzw. in den *International Critical Tables* zusammengestellt. Wir haben uns ferner zunächst auf rein wässerige Lösungen beschränkt, da die Konstanten in anderen Lösungsmitteln nur spezielleres Interesse besitzen und außerdem stets wesentlich unsicherer sind. Deshalb blieben auch alle Arbeiten unberücksichtigt, in denen die Konstanten in Wasser unter Zusatz eines anderen Lösungsmittels (z.B. unter Zusatz von Äthanol zur Erhöhung der Löslichkeit) gemessen wurden. Eine Erweiterung der Tabellen auf Basen in wässeriger Lösung ist geplant.

Den eigentlichen Tabellen wird im Abschnitt I eine kritische Diskussion der verschiedenen Meßverfahren vorangestellt, auf die in jedem Fall zurückverwiesen werden kann. Abschnitt II enthält die notwendige Zeichenerklärung für die Benutzung der Tabellen, Abschnitt III Erläuterungen über den Anordnungsplan, Abschnitt IV die Tabellenwerte, Abschnitt V die zugehörigen Literaturangaben.

I. SURVEY OF METHODS OF MEASUREMENT

1. GENERAL REMARKS ON THE DISSOCIATION OF ACIDS IN WATER

The "dissociation" of an acid involves a protolytic reaction with the base, water. For an acid, HA, such a reaction proceeds according to the equation

$$HA\,aq + nH_2O \rightleftharpoons A^-aq + H_3O^+aq \tag{1}$$

where "aq" denotes that the entities are hydrated. The equilibrium, is expressed by the relation

$$K' = \frac{[a_{A^-aq}][a_{H_3O^+aq}]}{[a_{HAaq}][a_{H_2O}{}^n]} \tag{2}$$

With small concentrations of electrolyte, a_{H_2O} is virtually constant, and if also the symbol "aq" is omitted for the sake of simplicity, equation (2) may be restated in the form

$$K \equiv K'a_{H_2O}{}^n = \frac{[a_{A^-}][a_{H_3O^+}]}{[a_{HA}]} = \frac{[c_{A^-}][c_{H_3O^+}]}{[c_{HA}]} \cdot \frac{f_{\pm}{}^2}{f_{HA}} \tag{3}$$

Strictly, therefore, K is a function of the acid concentration but the experimental errors in K are usually far larger than this effect; hence it suffices, at least for low concentrations, to describe the equilibrium (1) in terms of the virtual constant K.

Direct determination of the individual activities in equation (3) is in principle only possible for a_{AH} (e.g. by measurements of solubility). In the case of ions only $[c_{A^-}][c_{H_3O^+}]f_{\pm}{}^2$ can be evaluated. However, all the activity coefficients f are, by definition, equal to unity in the standard state, which is a solution of concentration 1 with the properties of a solution of infinite dilution, and it is possible to determine, for example, the classical dissociation constant, $K_c = [c_{A^-}][c_{H_3O^+}]/[c_{HA}]$ at finite concentrations as a function of the ionic strength and to extrapolate to $I = 0$. As a rule, the Debye–Hückel equation (sometimes in extended form) for $f_{\pm}$ is utilized; with equation (3) this leads to

$$\log K_c = \log K + 2A\sqrt{I} \tag{4}$$

on the assumption that f_{HA} is unity. The Debye–Hückel equation only states the variation of $f_{\pm}$ with the ionic strength in a solvent of constant composition. However, the presence of the undissociated part of a weak electrolyte alters the properties of the solvent, and therefore A is also a function of the concentration of the undissociated acid. The case of acetic acid solutions in pure water is a clear example. Thus, if K_c is measured as a function of the ionic strength, its relationship with K may be expressed by

$$\log K = \log K_c + 2 \log f_{\pm} \tag{5}$$

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I. ÜBERBLICK ÜBER DIE MESSMETHODEN

1. ALLGEMEINE ÜBERLEGUNGEN ZUR DISSOZIATION VON SÄUREN IN WASSER

Die "Dissoziation" einer Säure besteht in der protolytischen Reaktion mit der Base Wasser. Die Reaktionsgleichung lautet für eine Säure HA:

$$HA\,aq + nH_2O \rightleftharpoons A^-aq + H_3O^+aq \tag{1}$$

"aq" soll andeuten, daß die Reaktionsteilnehmer hydratisiert sind. Im Gleichgewicht gilt:

$$K' = \frac{[a_{A^-aq}][a_{H_3O^+aq}]}{[a_{HAaq}][a_{H_2O}{}^n]}. \tag{2}$$

Bei kleinen Konzentrationen des Elektrolyten wird a_{H_2O} praktisch konstant sein. Wenn die Zeichen "aq" der Einfachheit halber weggelassen werden, gilt also

$$K \equiv K' a_{H_2O}{}^n = \frac{[a_{A^-}][a_{H_3O^+}]}{[a_{HA}]} = \frac{[c_{A^-}][c_{H_3O^+}]}{[c_{HA}]} \cdot \frac{f_\pm{}^2}{f_{HA}} \tag{3}$$

Streng genommen sind die K konzentrationsabhängig, da indessen die experimentellen Fehler in K meistens weit größer sind als dieser Effekt, genügt es, wenigstens bei kleinen Konzentrationen, K zur Beschreibung des Gleichgewichtes (1) anzugeben.

Eine direkte Bestimmung der Einzelaktivitäten in Gl. (3) ist prinzipiell nur bei a_{AH} möglich (z.B. durch Löslichkeitsmessungen). Im Falle der Ionen läßt sich nur $[c_{A^-}][c_{H_3O^+}]f_\pm{}^2$ messen. Da aber alle Aktivitätskoeffizienten f nach der üblichen Normierung auf eine Lösung der Konzentration 1 mit den Eigenschaften einer unendlich verdünnten Lösung bei $c \to 0$ gleich eins werden, ermittelt man z.B. die "klassische Dissoziationskonstante" $K_c = [c_{A^-}][c_{H_3O^+}]/[c_{HA}]$ als Funktion der Ionenstärke $\mathcal{J}$ und extrapoliert auf $\mathcal{J} = 0$. Meistens bedient man sich dazu der (u.U. erweiterten) Debye–Hückel'schen Gleichung für $f_\pm$, die zusammen mit Gl. (3) ergibt

$$\log K_c = \log K + 2A\sqrt{\mathcal{J}} \tag{4}$$

f_{HA} wird dabei als 1 angenommen. Die D.-H.-Gleichung gibt nur die Variation von $f_\pm$ mit der Ionenstärke in einem Lösungsmittel konstanter Zusammensetzung an. Die Anwesenheit des undissoziierten Anteils des schwachen Elektrolyten verändert aber die Eigenschaften des Lösungsmittels. A ist demnach noch abhängig von der Konzentration der undissoziierten Säure. Das Beispiel von Essigsäure in reinem Wasser möge das verdeutlichen. Man mißt K_c als Funktion der Ionenstärke. Der Zusammenhang mit K ist gegeben durch

$$\log K = \log K_c + 2 \log f_\pm \tag{5}$$

if it is assumed that $\log f_{HA}=0$. The $f_{\pm}$ values thus refer to pure water as the solvent. The D.–H. equation

$$\log f_{\pm}^{*} = -A^{*}\sqrt{I} \tag{6}$$

however, only states the variation of $f_{\pm}^{*}$ with $\sqrt{I}$ in the actual solvent (H_2O + undissociated acetic acid) where A^{*} is the D.–H. constant corresponding to this solvent mixture. Since the dielectric constant of such a mixture (without the ions of acetic acid) is not known, A^{*} cannot be calculated. The relationship between f^{*} and f may be deduced from thermodynamic considerations; thus

$$\log f_{\pm} = \log (f_{\pm})_0 + \log f_{\pm}^{u} \tag{7}$$

where $\log (f_{\pm})_0$ ($I \to 0$; $c_{HA}=$ const.) is known as the "primary medium effect"[2]. The application of the D.–H. equation to equation (5) then gives:

$$\log K = \log K_c + 2 \log (f_{\pm})_0 - 2A^{*}\sqrt{I} \tag{8}$$

where not only $\log (f_{\pm})_0$ but also A^{*} depends on c_{HA}. Since both quantities are unknown, it is necessary to proceed in the following way. Approximately, $\log f_{\pm}$ is given by

$$\log f_{\pm} \simeq -A\sqrt{I} \tag{9}$$

where A is the D.–H. constant for pure water. $\log f_{\pm}$ is replaced by $\log f_{\pm}^{\circ}$, for which the expression

$$\log f_{\pm}^{\circ} = \lim_{\substack{c_{HA}\to 0 \\ I=\text{const}}} \log f_{\pm}^{*}$$

is valid. The process is thus approximate, because

$$\log (f_{\pm})_0 + \log f_{\pm}^{u} \neq \log f_{\pm}^{\circ} \tag{10}$$

as long as $c_{HA} \neq 0$, as is readily inferred from equation (7). This approximation results in deviations from the equation

$$\log K_c = \log K - 2A\sqrt{I}$$

at higher concentrations of acetic acid. This effect is known as the *medium effect*[1,2]. According to investigations by MacInnes and Shedlovsky[1], it appears in solutions of acetic acid at concentrations greater than ~0·01N.

2. DETERMINATION OF DISSOCIATION CONSTANTS BY CONDUCTANCE MEASUREMENTS

Only free ions can participate in the transport of current through a solution of an electrolyte, hence the degree of dissociation, α, of an electrolyte can be deduced from the observed conductance. A valid expression for the migration of ions in the electrical field is clearly essential and the dependence of the equivalent conductance on the total concentration c_0 of the electrolyte may be stated as

$$\Lambda_c = \Lambda_0 f_{\pm} \alpha \tag{11}$$

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wenn $\log f_{HA}=0$ angenommen wird. Die $f_{\pm}$ sind dabei normiert auf reines Wasser als Lösungsmittel. Die D.-H.-Gleichung

$$\log f_{\pm}^{*} = -A^{*}\sqrt{\bar{J}} \tag{6}$$

gibt jedoch nur die Variation der $f_{\pm}^{*}$ mit $\sqrt{\bar{J}}$ im Lösungsmittel (H_2O + undiss. Essigsäure) an; A^{*} ist der Wert für dieses Mischlösungsmittel. Da die DK solcher Mischungen (ohne Essigsäureionen!) nicht bekannt ist, kann A^{*} nicht berechnet werden. Der Zusammenhang zwischen f^{*} und f folgt aus thermodynamischen Betrachtungen zu

$$\log f_{\pm} = \log (f_{\pm})_0 + \log f_{\pm}^{*} \tag{7}$$

wobei $\log (f_{\pm})_0$ ($\bar{J}\to 0$; $c_{HA}=\text{const.}$) als sog. "primärer Mediumeffekt"[2] bezeichnet wird. Die exakte Anwendung der D.-H.-Gleichung auf die Gleichung für $\log K$ wäre also:

$$\log K = \log K_c + 2\log (f_{\pm})_0 - 2A^{*}\sqrt{\bar{J}} \tag{8}$$

worin sowohl $\log (f_{\pm})_0$ als auch A^{*} von c_{HA} abhängen. Da beide Größen unbekannt sind, geht man praktisch folgendermaßen vor: Man approximiert $\log f_{\pm}$ nach

$$\log f_{\pm} \simeq -A\sqrt{\bar{J}} \tag{9}$$

worin A der Wert für reines Wasser ist. Man ersetzt also $\log f_{\pm}$ durch $\log f_{\pm}^{\circ}$, für das gilt

$$\log f_{\pm}^{\circ} = \lim_{\substack{c_{HA}\to 0 \\ \bar{J}=\text{const}}} \log f_{\pm}^{*}$$

Approximativ ist das Verfahren deshalb, weil

$$\log (f_{\pm})_0 + \log f_{\pm}^{*} \neq \log f_{\pm}^{\circ} \tag{10}$$

solange $c_{HA}\neq 0$, wie leicht aus Gleichung (7) folgt. Diese Näherung hat zur Folge, daß bei höheren Essigsäurekonzentrationen Abweichungen von der Gleichung

$$\log K_c = \log K - 2A\sqrt{\bar{J}}$$

auftreten. Man bezeichnet diesen Effekt als *Mediumeffekt*[1,2]. Nach Untersuchungen von MacInnes und Shedlovsky[1] tritt er bei Essigsäurelösungen bei etwa $c>0{,}01$ in Erscheinung.

2. BESTIMMUNG DER DISSOZIATIONSKONSTANTEN AUS LEITFÄHIGKEITSMESSUNGEN

Da am Stromtransport durch eine Elektrolytlösung nur die freien Ionen teilnehmen, kann aus der Leitfähigkeit auf deren Dissoziationsgrad α geschlossen werden. Voraussetzung dafür ist, daß ein gültiger Ansatz für die Bewegung der Ionen im elektrischen Feld vorliegt. Die Abhängigkeit der Äquivalentleitfähigkeit von der Gesamtkonzentration c_0 des Elektrolyten läßt sich darstellen durch

$$\Lambda_c = \Lambda_0 f_A \alpha \tag{11}$$

where Λ_0 is the limiting value at $c_0=0$, obtained by extrapolating the measured values, f_Λ is the so-called conductance coefficient which takes into account the effect of interionic attraction, and α is the degree of dissociation. Conductance measurements thus yield values of the product αf_Λ, and if f_Λ is known, it is possible to calculate α and hence the classical dissociation constant, K_c:

$$K_c = \frac{[c_{A^-}][c_{H_3O^+}]}{[c_{HA}]} = \frac{\alpha^2}{1-\alpha} c_0 \qquad (12)$$

From equations (12) and (4), the thermodynamic constant K is obtained by extrapolation to $\sqrt{I}=0$. The degree of dissociation can be ascertained from equation (11) in various ways.

(a) Method of Davies[3]

f_Λ is calculated by successive approximations from the Debye-Hückel-Onsager equation in the form

$$f_\Lambda = 1 - \frac{A}{\Lambda_0} \sqrt{\alpha c_0} \qquad (13)$$

First f_Λ is made equal to 1, and from equation (11) a first value, α_1, is obtained, which is then inserted in (13) to give $(f_\Lambda)_1$. This process is continued until f_Λ is no longer changed. Two assumptions are made in the method:

(1) It is assumed that the Debye-Hückel-Onsager equation for f_Λ is quantitatively exact, i.e. the appropriate limiting gradient A is that given by theory.

(2) Λ_0 is assumed to be known.

Both assumptions may involve uncertainties which may become important with solvents of small dielectric constant. Λ_0 can be determined, on the basis of Kohlrausch's law of independent ionic migration, from Λ_0 values for related strong electrolytes; e.g.

$$\Lambda_{0,HA} = \Lambda_{0,NaA} + \Lambda_{0,HCl} - \Lambda_{0,NaCl} \qquad (14)$$

The Λ_0 values on the right side are obtained by graphical or analytical extrapolation of the measured values to $\sqrt{c}=0$, and $\Lambda_{0,HA}$, being the difference between these quantities, is therefore less accurately known in certain circumstances.

(b) Method of MacInnes[4]

The quantity $\Lambda_c \equiv f_\Lambda \Lambda_0$ is determined directly and α is then calculated from equation (11):

$$\alpha = \frac{\Lambda_c}{\Lambda_c} \qquad (15)$$

The quantity Λ_c is the conductance of a weak electrolyte, if it were completely dissociated, but at the actual ionic concentration to which Λ_c refers.

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Λ_0 ist der durch Extrapolation der Meßwerte zugängliche Grenzwert bei $c_0 = 0$, f_Λ der sog. Leitfähigkeitskoeffizient, der die interionische Wechselwirkung berücksichtigt, α der Dissoziationsgrad. Leitfähigkeitsmessungen liefern also αf_Λ. Bei Kenntnis von f_Λ kann daraus α berechnet werden, und damit die klassische Dissoziationskonstante K_c:

$$K_c = \frac{[c_{A^-}][c_{H_3O^+}]}{[c_{HA}]} = \frac{\alpha^2}{1-\alpha} c_0 \tag{12}$$

aus der sich wieder mittels (4) die thermodynamische Konstante K durch Extrapolation auf $\sqrt{\bar{J}} = 0$ ergibt. Der Dissoziationsgrad kann aus Gl. (11) auf verschiedene Weise ermittelt werden.

(a) Methode nach Davies[3]

f_Λ wird nach der Debye-Hückel-Onsager-Gleichung

$$f_\Lambda = 1 - \frac{A}{\Lambda_0} \sqrt{\alpha c_0} \tag{13}$$

mit Hilfe eines Näherungsverfahrens berechnet. Man setzt zunächst $f_\Lambda = 1$ und erhält aus Gl. (11) ein erstes α_1, das in (13) eingesetzt ein erstes $(f_\Lambda)_1$ liefert. Dieses Verfahren wird solange fortgesetzt, bis sich f_Λ nicht mehr ändert. Bei dieser Methode werden zwei Annahmen gemacht:

(1) Die Debye-Hückel-Onsager-Gleichung für f_Λ gilt quantitativ, also auch die Grenzneigung A ist die von der Theorie vorgeschriebene.

(2) Λ_0 ist bekannt.

Beide Annahmen bedingen gewisse Unsicherheiten, die bei Lösungsmitteln kleiner D.K. erheblich sein können. Man ermittelt Λ_0 nach dem Kohlrausch'schen Gesetz der unabhängigen Ionenwanderung aus den Werten Λ_0 für starke Elektrolyte: also z.B.

$$\Lambda_{0,HA} = \Lambda_{0,NaA} + \Lambda_{0,HCl} - \Lambda_{0,NaCl} \tag{14}$$

Da die Λ_0 der rechten Seite durch graphische oder rechnerische Extrapolation der Meßwerte auf $\sqrt{c} = 0$ erhalten werden, ist $\Lambda_{0,HA}$ als Differenz dieser Größen u.U. nicht sehr genau.

(b) Methode nach MacInnes[4]

Die Größe $\Lambda_c \equiv f_\Lambda \Lambda_0$ wird direkt ermittelt und damit aus Gl. (11) α berechnet:

$$\alpha = \frac{\Lambda_c}{\Lambda_c} \tag{15}$$

Die Rechengröße Λ_c wäre die Leitfähigkeit des schwachen Elektrolyten, wenn dieser vollständig dissoziiert wäre, bei der ionalen Konzentration, die in der untersuchten Lösung vorliegt.

The assumption is made that Kohlrausch's law (14) remains valid at the finite concentrations used, so that

$$\Lambda_{c,\mathrm{HA}} = \Lambda_{c,\mathrm{NaA}} + \Lambda_{c,\mathrm{HCl}} - \Lambda_{c,\mathrm{NaCl}} \tag{16}$$

The Λ_c values on the right side are therefore the equivalent conductances of the strong electrolytes, NaA, *etc.*, at the same ionic concentrations c that are present in the solution under investigation. At this stage α is unknown, but this is also true for $\alpha c_0 = c$. Hence, it is necessary to make several approximations which, however, usually converge rapidly. The application of this method requires that Λ_c of the strong electrolytes in equation (16) be known as a function of ionic concentration; the value corresponding to the concentration c can then be interpolated either graphically or analytically by use of the appropriate function $\Lambda_c = f(I)$, e.g. from Onsager's equation. According to empirical measurements Kohlrausch's law (16) can be assumed to be valid below $I = 2 \times 10^{-3}$. Since the method does not rely on the validity of the Debye–Hückel–Onsager limiting law, expressed as the limiting gradient as $I \to 0$, it seems possible to apply the method even beyond the range of validity of this limiting equation, up to $I \simeq 10^{-2}$. According to investigations by MacInnes, Shedlovsky and Longworth[5] on solutions containing the chlorides of H, Li, Na and K, the deviations from Kohlrausch's law are very small up to concentrations of 0·02, and this is of importance in the determination of large K values (see the paragraph below on the method of Shedlovsky).

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(c) Method of Fuoss and Kraus[6]

This method utilizes only the conductance measurements relating to the weak electrolytes themselves for the determination of K. The calculations involve the use of the Debye–Hückel–Onsager equation in the form

$$\Lambda_c = \alpha(\Lambda_0 - A\sqrt{\alpha c_0}) \tag{17}$$

which is a cubic equation in α. If an additional quantity z is defined

$$z \equiv A\sqrt{\frac{c_0 \Lambda_c}{\Lambda_0^3}} \tag{18}$$

then equation (17) reduces to[7]

$$\alpha = \frac{\Lambda_c}{\Lambda_0} F(z) \tag{19}$$

where $F(z)$ is a function of z which has been tabulated for all likely values of z. Together with the expression for K,

$$K = \frac{\alpha^2 c_0}{1-\alpha} f_z^2 \tag{20}$$

this leads to the further equation

$$\frac{F(z)}{\Lambda_c} = \frac{1}{\Lambda_0} + \frac{c_0 \Lambda_c f_z^2}{K \Lambda_0^2} \cdot \frac{1}{F(z)} \tag{21}$$

Man geht dazu von der Annahme aus, daß das Kohlrausch'sche Gesetz (14) auch bei endlichen Konzentrationen gültig bleibt, so daß

$$\Lambda_{\epsilon,\mathrm{HA}} = \Lambda_{\epsilon,\mathrm{NaA}} + \Lambda_{\epsilon,\mathrm{HCl}} - \Lambda_{\epsilon,\mathrm{NaCl}} \tag{16}$$

Die Λ_ϵ-Werte der rechten Seite sind dabei die Leitfähigkeiten der starken Elektrolyte NaA *etc.* bei der gleichen ionalen Konzentration ϵ, die in der untersuchten Lösung vorliegt. Da α vorläufig unbekannt ist, gilt dies auch für $\alpha c_0 = \epsilon$. Deshalb müssen einige Näherungen gemacht werden, die indessen meistens schnell konvergieren. Die Anwendung des Verfahrens verlangt zunächst die Kenntnis der Λ_ϵ der starken Elektrolyte in Gl. (16) in Abhängigkeit von der Konzentration. Die Interpolation auf die Konzentration ϵ wird entweder graphisch oder mit einer analytischen Darstellung der Funktion $\Lambda_\epsilon = f(\mathcal{J})$ z.B. mit der Onsager-Gleichung durchgeführt. Die Gültigkeit des Kohlrausch'schen Gesetzes (16) kann nach empirischen Messungen unterhalb $\mathcal{J} = 2 \cdot 10^{-3}$ vorausgesetzt werden. Da das Verfahren die Gültigkeit des Debye–Hückel–Onsager-Grenzgesetzes einschließlich der Grenzneigung nicht voraussetzt, scheint es möglich zu sein, es auch noch außerhalb des Geltungsbereiches dieser Grenzgleichung anzuwenden, also etwa bis $\mathcal{J} \simeq 10^{-2}$. Nach Untersuchungen von MacInnes, Shedlovsky und Longworth[5] an Lösungen der Chloride von H, Li, Na und K sind die Abweichungen vom Kohlrausch'schen Gesetz bis zu Konzentrationen von 0,02 sehr gering. Dieser Umstand ist von Wichtigkeit bei der Ermittlung von großen K-Werten (vgl. den Abschnitt "Methode nach Shedlovsky").

(c) Methode von Fuoss und Kraus[6]

Dieses Verfahren benutzt zur Ermittlung von K nur Leitfähigkeitsmessungen an Lösungen des schwachen Elektrolyten selbst. Es handelt sich dabei um ein Rechenverfahren zur Auswertung der Debye–Hückel–Onsager-Gleichung

$$\Lambda_\epsilon = \alpha(\Lambda_0 - A\sqrt{\alpha c_0}) \tag{17}$$

die in Bezug auf α dritten Grades ist. Mit der Definition

$$z \equiv A\sqrt{\frac{c_0 \Lambda_\epsilon}{\Lambda_0{}^3}} \tag{18}$$

ergibt sich durch Umrechnen[7]

$$\alpha = \frac{\Lambda_\epsilon}{\Lambda_0} F(z) \tag{19}$$

worin $F(z)$ eine Funktion von z ist, die für alle in Frage kommenden Werte von z tabelliert ist. Zusammen mit dem Ausdruck für K

$$K = \frac{\alpha^2 c_0}{1-\alpha} f_\pm{}^2 \tag{20}$$

erhält man die Gleichung

$$\frac{F(z)}{\Lambda_\epsilon} = \frac{1}{\Lambda_0} + \frac{c_0 \Lambda_\epsilon f_\pm{}^2}{K \Lambda_0{}^2} \cdot \frac{1}{F(z)} \tag{21}$$

A first value, z_1, is then calculated from an approximate value of Λ_0 and this leads to a first approximation for α by means of equation (19). A first approximation for $f_\pm$ at this ionic concentration is also calculated from the Debye–Hückel equation relating to mean activity coefficients. This procedure is repeated for all the points measured and the values for $F(z)/\Lambda_c$ are plotted against $c_0\Lambda_c f_\pm^2/F(z)$. The ordinate $1/\Lambda_0$ of the straight line obtained yields a second approximation for Λ_0. The process is repeated until Λ_0 is no longer altered. K can then be calculated from the slope of the linear extrapolation of equation (21).

This method thus requires no assumptions based on the validity of the limiting laws for $f_\pm$ and for Λ_c. Since its accuracy has been demonstrated for a wide range of systems, reliable values of K can be expected from this method, provided that the measurements lie within the ionic concentration range of the limiting relations.

(d) Method of Shedlovsky[8]

This method is strictly analogous to the aforementioned method of Fuoss and Kraus with the difference that the equation proposed by Shedlovsky,

$$\Lambda_c = \Theta(\Lambda_0 - A\frac{\Lambda_c}{\Lambda_0}\sqrt{\Theta c_0}) \tag{22}$$

where Θ also signifies the degree of dissociation, is applied instead of the Onsager equation. In a similar way, the quantity

$$\Theta = \frac{\Lambda_c}{\Lambda_0}S(z) \tag{23}$$

is used, where z is again defined by equation (18) and $S(z)$ is a function of z only[9]. Substitution of equation (23) into equation (20) yields

$$\frac{1}{\Lambda_c S(z)} = \frac{1}{\Lambda_0} + \frac{c_0\Lambda_c f_\pm^2 S(z)}{K\Lambda_0^2} \tag{24}$$

Equation (24) is used in precisely the same way as equation (21). Although Θ is characterized as the degree of dissociation in the calculations[10] (e.g. when substituted in the expression for K), the authors have computed, from the expression for Λ_c, the difference between Θ and α, i.e.,

$$\alpha = \Theta[1 + z(F^{-3/2}S^{-1} - S^{-1/2})] \tag{25}$$

In fact, therefore, this method yields values for K different from those obtained by the method of Fuoss and Kraus. The authors state that "the difference is a consequence of the difference between Θ and α", but this would seem to introduce a contradiction, since if Θ is interpreted as the degree of dissociation, then

$$\Theta \equiv \alpha \tag{26}$$

and the difference between the two methods lies in the use of two different equations for Λ_c. Since both methods aim in principle at a solution of these equations for the degree of dissociation, the problem is to decide which is the more reliable equation for Λ_c.

Man berechnet nun mit einem Näherungswert für Λ_0 einen ersten Wert z_1, der nach Gl. (19) zu einer ersten Näherung für α führt. Nach der Debye-Hückel'schen Gleichung für den mittleren Aktivitätskoeffizienten wird eine erste Näherung für $f_\pm$ bei dieser Ionenkonzentration berechnet. Das wird für alle Meßpunkte wiederholt, und die Werte für $F(z)/\Lambda_c$ werden gegen $c_0\Lambda_c f_\pm^2/F(z)$ aufgetragen. Die dabei erhaltene Gerade liefert in ihrem Ordinatenabschnitt $1/\Lambda_0$ eine zweite Näherung für Λ_0. Das Verfahren wird solange wiederholt, bis sich Λ_0 nicht mehr ändert. Aus der Steigung der Extrapolationsgeraden kann dann K berechnet werden.

Dieses Verfahren benötigt also keinerlei Annahmen außer der Gültigkeit der Grenzgesetze für $f_\pm$ und für Λ_c. Da deren Richtigkeit an Hand eines sehr großen Untersuchungsmaterials als sicher anzusehen ist, sind nach dieser Methode zuverlässige K-Werte zu erwarten, sofern die Messungen im ionalen Konzentrationsbereich der Grenzgesetze liegen.

(d) Methode nach Shedlovsky[8]

Diese Methode ist völlig analog zu der eben besprochenen von Fuoss und Kraus mit dem Unterschied, daß hier statt der Onsager-Gleichung (17) die von Shedlovsky vorgeschlagene Gleichung verwendet wird

$$\Lambda_c = \Theta\left(\Lambda_0 - A\frac{\Lambda_c}{\Lambda_0}\sqrt{\Theta c_0}\right) \tag{22}$$

worin Θ ebenfalls als Dissoziationsgrad bezeichnet wird. Für Θ gilt nach analoger Rechnung

$$\Theta = \frac{\Lambda_c}{\Lambda_0} S(z) \tag{23}$$

wobei z wieder durch Gl. (18) definiert ist und $S(z)$ eine Funktion nur von z ist[9]. Gl. (23) in Gl. (20) eingesetzt ergibt

$$\frac{1}{\Lambda_c S(z)} = \frac{1}{\Lambda_0} + \frac{c_0 \Lambda_c f_\pm^2 S(z)}{K\Lambda_0^2} \tag{24}$$

Die Gl. (24) wird ganz analog der Gl. (21) angewendet. Obwohl in der Rechnung[10] Θ als Dissoziationsgrad charakterisiert ist (z.B. beim Einsetzen in den Ausdruck für K), berechnen die Autoren durch Gleichsetzen der Ausdrücke für Λ_c den Unterschied zu α:

$$\alpha = \Theta[1 + z(F^{-3/2}S^{-1} - S^{-1/2})] \tag{25}$$

Tatsächlich liefert diese Methode auch andere K-Werte als die Methode von Fuoss und Kraus. Die Autoren schreiben dazu: "The difference is a consequence of the difference between Θ and α". Hier scheint ein Widerspruch vorzuliegen. Wenn man Θ als Dissoziationsgrad auffaßt, ist:

$$\Theta \equiv \alpha \tag{26}$$

und der Unterschied in den beiden Verfahren liegt in der Verwendung zweier verschiedener Gleichungen für Λ_c. Da beide Methoden im Prinzip eine Lösung dieser Gleichungen für den Dissoziationsgrad bezwecken, mündet die Frage danach, welche die richtige Konstante K liefert, in die nach der Zuverlässigkeit der Gleichungen für Λ_c.

Whereas numerous investigations of the validity of the Onsager equation show the upper concentration limit as $c \simeq 2 \times 10^{-3}$, equation (22) of Shedlovsky remains valid at considerably higher ionic concentrations[10]:

$$\Lambda_c = \Lambda_0 - A\frac{\Lambda_c}{\Lambda_0}\sqrt{c} \tag{27}$$

The method discussed here, therefore, seems preferable in every case. For $K < 10^{-3}$ both methods yield virtually the same[10] values of K. However, for $K > 10^{-3}$, the following considerations must be taken into account. For large K values the degree of dissociation, even at high acid concentrations, c_{HA}, is relatively great, and there is, therefore, a concentration limit (determined by the precision of the measurement of Λ_c), below which α can no longer be experimentally differentiated from unity. This limiting concentration increases as K increases. If it lies outside the range of validity of equations (17) or (22), which form the basis of both methods, then obviously no reliable value for K can be expected. If, for example, Λ_c is measured with a certainty of 0·1 per cent, $f_A\alpha$ has at least the same error. The probable error may be taken as 0·3 per cent, in which case a value of $\alpha = 0{\cdot}997$ lies just on the limit of error. For a dissociation constant $K = 0{\cdot}3$, this corresponds to a concentration limit $c \simeq 0{\cdot}001$. In the chosen example, this is the smallest concentration at which K can be experimentally differentiated from ∞; but this is also about the limit of validity of the Onsager equation. Therefore, if equation (27) can be verified in some cases at higher concentrations, then *for large dissociation constants*, the method of Shedlovsky must be regarded as the more reliable.

3. DETERMINATION OF DISSOCIATION CONSTANTS BY ELECTROMETRIC MEASUREMENTS

In principle, it is always possible to determine dissociation constants from the E.M.F. of galvanic cells where hydrogen ions participate in one of the potential-determining electrode reactions. An important consideration in the assessment of the various methods is whether or not the cells possess a liquid junction potential. From the outset it should be realized that a fundamental uncertainty in derived dissociation constants is introduced by the existence of diffusion potentials, the magnitude of which usually cannot be stated. This follows from the fact that it is not possible to determine diffusion potentials without making additional non-thermodynamic assumptions.

For cells without transport, i.e. without liquid junctions of the type

$$\mathrm{Pt(H_2)|HA,NaA,NaCl}\,\underset{x}{|}\,\mathrm{HA,NaA,NaCl|AgCl|Ag} \tag{28}$$

there is in fact a diffusion potential at x but it is very small because of the negligible solubility of the silver chloride. When K is calculated from the E.M.F.'s of such cells, any diffusion potential is, in any case, eliminated, for it also occurs in the determination of the standard E.M.F. of these cells. The E.M.F. of cell (28) can be expressed as:

$$E = E_0 - \frac{RT}{F}\ln\left(a_{H_3O^+}\cdot a_{Cl^-}\right) \tag{29}$$

Während die sehr zahlreichen Untersuchungen über die Gültigkeit der Onsager-Gleichung als Grenze $c \simeq 2 \cdot 10^{-3}$ angeben, soll die Gleichung (22) von Shedlovsky noch bei beträchtlich höheren ionalen Konzentrationen gültig bleiben[10]:

$$\Lambda_c = \Lambda_0 - A \frac{\Lambda_c}{\Lambda_0} \sqrt{c} \tag{27}$$

Danach wäre in jedem Fall die hier besprochene Methode vorzuziehen. Bei $K < 10^{-3}$ liefern beide Verfahren praktisch die gleichen[10] Werte für K. Bei $K > 10^{-3}$ aber ist noch folgendes zu beachten. Da bei größeren K die Dissoziation auch bei hohen Konzentrationen c_{HA} relativ groß ist, wird es offenbar eine (durch die erreichte Genauigkeit in der Messung von Λ_c bestimmte) Konzentration geben, unterhalb deren α experimentell nicht mehr von 1 zu unterscheiden ist. Diese Grenzkonzentration wird umso größer sein, je größer K ist. Wenn nun diese Grenzkonzentration außerhalb des Gültigkeitsbereiches der den beiden Methoden zu Grunde liegenden Gleichungen (17) bzw. (22) liegt, sind offenbar keine zuverlässigen Aussagen über K mehr zu erwarten. Wenn z.B. Λ_c mit einer Sicherheit von 0,1 Prozent gemessen ist, so hat $f_\Lambda \alpha$ mindestens den gleichen Fehler. Es sei angenommen, daß er 0,3 Prozent ist. Dann liegt ein $\alpha = 0{,}997$ gerade noch an der Fehlergrenze. Bei einer Konstanten $K = 0{,}3$ ist das bei etwa $c \simeq 0{,}001$ der Fall. Das wäre also bei dem gewählten Beispiel die kleinste Konzentration, bei der eine experimentelle Unterscheidung des K von ∞ möglich wäre. Das ist aber etwa die Gültigkeitsgrenze für die Onsager-Gleichung. Wenn also auch Gl. (27) nur in einigen Fällen bei höheren Konzentrationen verifiziert würde, so ist dem Verfahren von Shedlovsky *bei großen Konstanten* doch die größere Zuverlässigkeit zuzusprechen.

3. BESTIMMUNG DER DISSOZIATIONSKONSTANTEN AUS ELEKTROMETRISCHEN MESSUNGEN

Aus der E.M.K. von galvan. Zellen, an deren stromlieferndem Vorgang Wasserstoffionen beteiligt sind, müssen sich prinzipiell Dissoziationskonstanten bestimmen lassen. Wesentlich für die Beurteilung der einzelnen Verfahren ist die Frage, ob es sich um Zellen mit oder ohne Diffusionspotentiale handelt. Von vornherein ist zu sagen, daß bei Vorhandensein von Diffusionspotentialen in die Dissoziationskonstanten eine prinzipielle Unsicherheit eingeht, über deren Größe sich allgemein nichts aussagen läßt. Das rührt daher, daß es nicht möglich ist, Diffusionspotentiale ohne zusätzliche nichtthermodynamische Annahmen zu ermitteln.

Bei den sog. Zellen ohne Diffusionspotential vom Typ

$$\mathrm{Pt(H_2)|Ha,NaA,NaCl\,\underset{x}{\|}\,HA,NaA,NaCl|AgCl|Ag} \tag{28}$$

liegt eigentlich auch ein Diffusionspotential bei x vor, das indessen wegen der Schwerlöslichkeit des Silberchlorids sehr klein ist. Bei der Berechnung von K aus Messungen an solchen Zellen verschwindet es durch Kompensation ganz, weil es auch bei der Ermittlung der Standard-E.M.K. dieser Zelle auftritt. Für die E.M.K. der Zelle (28) gilt

$$E = E_0 - \frac{RT}{F} \ln (a_{H_3O^+} a_{Cl^-}) \tag{29}$$

where E_0 is the standard E.M.F. of the cell

$$Pt(H_2)|HCl||AgCl|Ag \tag{30}$$

Thus, with the equation for ln K,

$$\ln K = \ln \frac{[m_{H_3O^+}][m_{A^-}]}{[m_{HA}]} \cdot \frac{f_{H_3O^+} f_{A^-}}{f_{HA}}, \tag{31}$$

we obtain

$$E - E_0 + \frac{RT}{F} \ln \frac{[m_{HA}][m_{Cl^-}]}{[m_{A^-}]} = -\frac{RT}{F}\left[\ln \frac{f_{H_3O^+} f_{Cl^-} f_{HA}}{f_{H_3O^+} f_{A^-}} + \ln K\right] \equiv -\frac{RT}{F} \ln K' \tag{32}$$

Measurements of the E.M.F. of such cells can thus be used for the calculation of K without additional assumptions[11]. Initial approximations (e.g. a provisional estimate of K) are required to calculate the concentration terms, but these converge rapidly for acids which are not too strong. For very weak acids, e.g. boric acid, the hydrolysis of the salts must be considered. Extrapolation of log K', plotted against I, to $I=0$ yields log K.

This method has the advantage that log K' varies only slightly with the ionic strength, but it demands very accurate measurements of E.M.F. because only the difference $(E-E_0)$ is involved. If the hydrogen electrode cannot be employed, it may be replaced by the quinhydrone electrode[12].

The use of E_0 values from the literature is only permissible if the reproducibility of the measured values is carefully checked. The potential of the silver-silver chloride electrode, for example, is strongly dependent on the amount of oxygen in the solution, and according to Güntelberg[13], variations of 0·5 mV may result from this effect. For this reason, subsequent evaluation of K from a superior, but inappropriate E_0 value may well lead to worse results than if a similarly inaccurate value had been used.

In general, the K values determined by this method may be counted among the most reliable known at present.

Another method of determining K from cells without liquid junctions involves measurements in unbuffered cells of the type

$$\underset{(M)}{Pt(H_2)|HA}, \underset{(m)}{NaCl}|AgCl|Ag \tag{33}$$

where it must be noted that the ratio m_{A^-}/m_{HA} cannot be calculated from the stoichiometric concentrations. The E.M.F. of this cell is expressed as

$$E = E_0 - \frac{RT}{F} \ln (m_{H_3O^+} m_{Cl^-} f_{\pm}^2) \tag{34}$$

E_0 is obtained from measurements on cell (30), and therefore the $f_{\pm}$ in equation (34) refers to the standard state of infinite dilution in pure water.

Two extrapolations are required (for details, see[13]) for the determination of K from measurements on such cells. The first extrapolation to $I=0$ is made with M constant and m variable. So long as $m_{H_3O^+} \ll M$, the ionic strength is thus varied with practically no alteration in the composition of

E_0 ist die Standard-E.M.K. der Zelle

$$\mathrm{Pt(H_2)|HCl|AgCl|Ag} \tag{30}$$

Zusammen mit

$$\ln K = \frac{\ln [m_{H_3O^+}][m_{A^-}]}{[m_{HA}]} \cdot \frac{f_{H_3O^+} f_{A^-}}{f_{HA}} \tag{31}$$

ergibt sich

$$E - E_0 + \frac{RT}{F} \ln \frac{[m_{HA}][m_{Cl^-}]}{[m_{A^-}]} = -\frac{RT}{F}\left[\ln \frac{f_{H_3O^+} f_{Cl^-} f_{HA}}{f_{H_3O^+} f_{A^-}} + \ln K\right] \equiv -\frac{RT}{F} \ln K' \tag{32}$$

E.M.K.-Messungen an solchen Zellen lassen sich also ohne zusätzliche Annahmen zur Berechnung von K verwenden[11]. Zur Berechnung des Konzentrationsterms werden Näherungen (z.B. mit einem angenäherten K) verwendet, die bei nicht zu starken Säuren sehr schnell konvergieren. Bei sehr schwachen Säuren (z.B. Borsäure) muß die Hydrolyse des Salzes berücksichtigt werden. Die Extrapolation von $\log K'$, gegen $\bar{J}$ aufgetragen, auf $\bar{J} = 0$ liefert $\log K$.

Das Verfahren hat den Vorteil, daß sich $\log K'$ nur wenig mit der Ionenstärke ändert. Dagegen erfordert die Methode wegen der Differenz $(E - E_0)$ sehr genaue Messungen der E.M.K. Wenn die Wasserstoffelektrode nicht verwendet werden kann, so kann sie durch die Chinhydronelektrode ersetzt werden[12].

Die Verwendung von E_0-Werten aus der Literatur ist nur zulässig, wenn man die Reproduzierbarkeit der Meßdaten sorgfältig prüft. Das Potential der Silber–Silberchlorid-Elektrode z.B. ist stark vom Sauerstoffgehalt der Lösung abhängig. Nach Untersuchungen von Güntelberg[13] können dabei Differenzen von 0,5 mV auftreten. Aus diesem Grunde kann eine nachträgliche Umrechnung von K-Werten mit einem besseren E_0 unter Umständen zu schlechteren Resultaten führen.

Prinzipiell zählen die nach dieser Methode bestimmten K-Werte[14] zu den zuverlässigsten, die bekannt sind.

Eine andere Art der Auswertung verlangen die Messungen an ungepufferten Zellen des Typs

$$\underset{(M)}{\mathrm{Pt(H_2)|HA}}\underset{(m)}{\mathrm{,NaCl|AgCl|Ag}} \tag{33}$$

da hier das Verhältnis m_{A^-}/m_{HA} nicht aus den stöchiometrischen Konzentrationen berechnet werden kann. Für die E.M.K. dieser Zelle gilt

$$E = E_0 - \frac{RT}{F} \ln m_{H_3O^+} m_{Cl^-} f_{\pm}^2 \tag{34}$$

Da E_0 aus Messungen der Zelle (30) erhalten wird, ist $f_{\pm}$ in Gl. (34) auf unendliche Verdünnung in reinem Wasser normiert.

Zur Bestimmung von K aus Messungen an solchen Zellen sind zwei Extrapolationen erforderlich (näheres darüber vgl.[15]). Die erste Extrapolation wird bei konstantem M und variablem m auf $\bar{J} = 0$ durchgeführt. Solange $m_{H_3O^+} \ll M$, wird dabei die Ionenstärke variiert, ohne daß sich die

the solvent. The values for the dissociation constant obtained by this extrapolation thus no longer include the effect of interionic attraction but include the effect on the medium of the undissociated acid, HA. A second extrapolation to $M=0$ yields the value of K. For this extrapolation the linear relation

$$\log K' = \log K + \text{const. } M \tag{35}$$

which has not been proved theoretically, is often used.

Extrapolation to $I=0$ requires that the concentration of the undissociated acid ($M-m_{H_3O^+}$) remains unaltered. The extrapolation must therefore be undertaken from relatively high ionic strengths. In the cited work of Harned and Owen[15] the minimum strength is $I=0{\cdot}02$. For the same reason, M must be relatively large (Harned and Owen state $M=0{\cdot}1$–$10{\cdot}2$ mole/1000g). Otherwise, the measured values must extend to the limit of the applicability of the Debye–Hückel equation. The K values obtained by this method are therefore somewhat uncertain, in comparison with those obtained from measurements in buffered cells. However, the method offers the advantage that some assessment can be made of the effect of the medium. Solvent or medium effects naturally also participate in measurements of cells of type (28); but they are not involved in the computations, since the extrapolation to $I=0$ can be made directly because the buffer compositions are known.

Measurements on cells of the type

$$\text{Pt}(H_2)|\text{test solution}|\text{satd KCl}|\text{reference electrode} \tag{36}$$

lead to the expression

$$\text{pH}' \equiv \frac{E-E_0'}{2{\cdot}30\,RT/F} \equiv \frac{E-E_0'}{k} \tag{37}$$

and pH', which is closely related to the normal pH value,

$$\text{pH} \equiv -\log a_{H_3O^+} \tag{38}$$

can thus be obtained. This pH' value contains the diffusion potentials which occur in cell (36). E_0' is therefore determined so that the measured pH' values approach the true pH values as closely as possible. For this purpose, standard solutions in the form of buffer solutions of an acid HA and one of its salts, e.g. NaA, are used. From the expression for the dissociation constant K of the acid HA, we obtain from (38),

$$\text{pH} = \text{p}K + \log\frac{m_{A^-}}{m_{HA}} + \log\frac{f_{A^-}}{f_{HA}} \tag{39}$$

If pH is replaced by the measured value pH' it follows that

$$\frac{E-E_0'}{k} = \text{p}K + \log\frac{m_{A^-}}{m_{HA}} + \log\frac{f_{A^-}'}{f_{HA}'} \tag{40}$$

The f' values are semi-empirical quantities, but by analogy with the Debye–Hückel equation, the expression can be re-written as:

$$\frac{E-E_0'}{k} - \log\frac{m_{A^-}}{m_{HA}} = {}^{*}\text{p}K - S\sqrt{I} \tag{41}$$

Zusammensetzung des Lösungsmittels praktisch ändert. Die durch diese Extrapolation erhaltenen Werte für die Dissoziationskonstante enthalten also nicht mehr den Einfluß der interionischen Wechselwirkung, wohl aber den Mediumeinfluß der undissoziierten Säure HA. Eine zweite Extrapolation auf $M=0$ führt zu K. Für diese zweite Extrapolation wird oft ein linearer Verlauf

$$\log K' = \log K + \text{const.}\, M \tag{35}$$

gefunden, der theoretisch nicht begründet ist.

Die Extrapolation auf $\mathcal{J}=0$ verlangt, daß sich die Konzentration der undissoziierten Säure $(M-m_{H_3O^+})$ dabei nicht ändert. Die Extrapolation muß deshalb von relativ großen Ionenstärken aus vorgenommen werden. In der zitierten Arbeit von Harned und Owen[15] ist minimal $\mathcal{J}=0{,}02$. Aus dem gleichen Grunde muß M relativ groß sein (bei Harned und Owen ist $M=0{,}1$–$10{,}2$ Mol/1000g). Andererseits müssen die Meßwerte bis zu den Konzentrationen reichen, bei denen die Debye–Hückel-Gleichung gilt.

Die nach diesem Verfahren erhaltenen K-Werte sind also gegenüber denen, die aus Messungen an gepufferten Zellen erhalten werden, etwas unsicherer. Die Methode bietet aber den Vorteil, daß mit ihr Aussagen über die Mediumeffekte möglich sind. Mediumeffekte spielen natürlich auch bei Messungen der Zellen des Typs (28) eine Rolle. Sie brauchen dort aber nicht berücksichtigt zu werden, weil die Extrapolation auf $\mathcal{J}=0$ wegen der Kenntnis des Pufferverhältnisses direkt möglich ist.

Messungen an Zellen des Typs

$$\text{Pt}(H_2)\,|\,\text{Testlösung}\,|\,\text{KCl gesätt.}\,|\,\text{Bezugselektrode} \tag{36}$$

führen zu dem Ausdruck

$$\text{pH}' \equiv \frac{E-E_0'}{2{,}30RT/F} \equiv \frac{E-E_0'}{k} \tag{37}$$

Dabei kann pH′ als Näherungswert für

$$\text{pH} \equiv -\log a_{H_3O^+} \tag{38}$$

aufgefaßt werden. Diese pH′-Werte enthalten die Diffusionspotentiale, die in (36) auftreten. E_0' wird so ermittelt, daß die gemessenen pH′-Werte sich dem wahren pH möglichst gut annähern. Dazu verwendet man Testlösungen in Form von Pufferlösungen aus einer Säure HA und einem ihrer Salze, z.B. NaA. Mit der Dissoziationskonstanten K der Säure HA wird aus (38)

$$\text{pH} = \text{p}K + \log\frac{m_{A^-}}{m_{HA}} + \log\frac{f_{A^-}}{f_{HA}} \tag{39}$$

Setzt man für pH den gemessenen Wert pH′ ein, so folgt

$$\frac{E-E_0'}{k} = \text{p}K + \log\frac{m_{A^-}}{m_{HA}} + \log\frac{f_{A^-}'}{f_{HA}'} \tag{40}$$

Die f' sind dabei empirische Größen. In Analogie zur Debye-Hückel-Gleichung wird nun der Ansatz gemacht

$$\frac{E-E_0'}{k} - \log\frac{m_{A^-}}{m_{HA}} = \text{p}K - S\sqrt{\mathcal{J}} \tag{41}$$

where S is an empirical quantity which may deviate by 10–25 per cent from the theoretical limiting gradient[16]. The value E_0' is then found by finding for which values the left side of equation (41) yields a linear function of $\sqrt{I}$ at small values of I. The E_0' determined in this way includes the diffusion potential between the reference electrode and the potassium chloride bridge. An additional method[17] for the determination of E_0' utilizes the Debye–Hückel equation for $\log f_{A^-}$ in place of the relation $-S\sqrt{I}$.

Another procedure employs a standard buffer solution[18] for the standardization of equation (32) if pH′ is measured by one of the above-mentioned methods; alternatively the true pH is established in the Debye–Hückel region from measurements in cells without diffusion potentials[19]. Approximate values for the dissociation constants of the acid being investigated can be calculated from the pH′ values thus obtained. For this purpose, it is assumed that the approximation

$$\mathrm{pH}' \simeq \mathrm{pH} \tag{42}$$

is sufficiently valid.

The equation

$$\mathrm{p}K_m' = \mathrm{pH}' - \log \frac{m_{A^-}}{m_{HA}} \tag{43}$$

is then obtained, m_{A^-}/m_{HA} being determined from the known buffer proportions of the solution by means of several approximations[20]. A first value for K_m' is calculated with the approximation $\mathrm{pH}' \simeq \mathrm{pH}$; a new value for m_{A^-}/m_{HA} is then calculated with this K_m' and so on. The extrapolation of the $\mathrm{p}K_m'$ values to infinite dilution yields $\mathrm{p}K'$. Another possibility is to calculate the apparent hydrogen ion concentration from pH′ by means of the Debye–Hückel equation for $\log f_\pm$ and to find $\log K_m'$ from this. Extrapolation of $-\log K_m'$ to $I=0$ then also leads to $\mathrm{p}K'$. The dissociation constants thus obtained[21] can therefore be considered as approximate values for the thermodynamic constant K. The use of equation (42) either neglects completely the liquid potential between the acid solution and the KCl salt-bridge (use of the Debye–Hückel equation for the determination of E_0') or neglects its dependence on the composition of the acid solution (determination of E_0' by means of equation (41) or calibration against a standard buffer). Better approximations for K' are obtained by calculation of the concentration terms of the diffusion potential, e.g. by the formula of Henderson[22]. The efficiency of the KCl salt-bridge in (36) in decreasing the diffusion potential can be checked by the method of Bjerrum[23]. For this purpose, the KCl concentration in the bridge is varied; the alterations observed in the E.M.F. are then the alterations in the diffusion potential. The errors caused by the latter can thus be estimated. It can therefore be seen that the dissociation constants determined by this method cannot in principle be claimed as highly satisfactory.

More reliable approximate values for K' can be obtained[24] from E.M.F. measurements on the cell:

$$\mathrm{Pt}(\mathrm{H_2})\,|\,\mathrm{HA,NaCl}\,|\,\text{satd KCl}\,|\,\mathrm{HCl,NaCl}\,|\,(\mathrm{H_2})\,\mathrm{Pt} \tag{44}$$

S ist ein empirischer Wert, der 10–25 Prozent von der theoretischen Grenzneigung abweichen kann[16]. Es wird nun der Wert E_0' durch Probieren gesucht, mit dem die linke Seite von Gl. (41) eine lineare Funktion von $\sqrt{\bar{J}}$ bei kleinen $\bar{J}$ ergibt. Das so bestimmte E_0' enthält das Diffusionspotential zwischen der Bezugselektrode und der Kaliumchloridbrücke. Eine weitere Methode[17] zur Bestimmung von E_0' benützt die Debye-Hückel-Gleichung für $\log f_{A^-}$ anstelle von $-S\sqrt{\bar{J}}$.

Andere Verfahren benützen Standardpuffer[18] zur Normierung von Gl. (32), deren pH′ nach einem der eben beschriebenen Verfahren gemessen wurden, oder deren wahres pH aus Messungen an Zellen ohne Diffusionspotential im Debye-Hückel-Gebiet ermittelt wurde[19]. Aus den so gewonnenen Werten pH′ können Näherungswerte für die Dissoziationskonstante der untersuchten Säure berechnet werden. Dazu nimmt man an, daß mit genügender Näherung gilt

$$\mathrm{pH}' \simeq \mathrm{pH} \tag{42}$$

Nun bildet man

$$\mathrm{p}K_m' = \mathrm{pH}' - \log \frac{m_{A^-}}{m_{HA}} \tag{43}$$

m_{A^-}/m_{HA} wird aus dem bekannten Pufferverhältnis der Testlösung durch einige Approximationen ermittelt[20]. Dazu wird mit der Näherung $\mathrm{pH}' \simeq \mathrm{pH}$ ein erster Wert für K_m' berechnet. Mit diesem K_m' kann m_{A^-}/m_{HA} neu berechnet werden und so fort. Die Extrapolation der $\mathrm{p}K_m'$-Werte auf unendliche Verdünnung liefert $\mathrm{p}K'$. Eine andere Möglichkeit ist, mit der Debye-Hückel-Gleichung für $\log f_\pm$ aus pH′ die scheinbare Wasserstoffionenkonzentration zu berechnen und damit $\log K_m'$ zu bilden. Die Extrapolation von $-\log K_m'$ auf $\bar{J}=0$ führt dann ebenfalls zu $\mathrm{p}K'$. Die so erhaltenen Dissoziationskonstanten[21] können also als Näherungswerte für die thermodynamische Konstante K' gelten. Die Anwendung der Gl. (42) vernachlässigt das Flüssigkeitspotential zwischen der Testlösung und der KCl-Brücke entweder ganz (Anwendung der Debye-Hückel-Gleichung zur Bestimmung von E_0') oder dessen Abhängigkeit von der Zusammensetzung der Testlösung (Ermittlung von E_0' nach Gl. (41) bzw. Eichung gegen Standardpuffer). Bessere Annäherung an K' wird durch Berechnung des Konzentrationsterms des Diffusionspotentials z.B. mit der Formel von Henderson[22] erreicht. Die Wirksamkeit der KCl-Brücke in (36) zur Verringerung der Diffusionspotentiale kann nach Bjerrum[23] nachgeprüft werden. Dazu variiert man die KCl-Konzentration in der Brücke. Die beobachteten Änderungen in der E.M.K. sind dann die Änderungen der Diffusionspotentiale. Daraus lassen sich die durch letztere verursachten Fehler abschätzen. Man sieht also, daß die auf diese Weise ermittelten Dissoziationskonstanten hohen Ansprüchen prinzipiell nicht gerecht werden können.

Zuverlässigere Näherungswerte für K' können aus E.M.K.-Messungen an folgender Zelle erhalten werden[24]

$$\mathrm{Pt(H_2)|HA,NaCl|KCl\ gesätt.|HCl,NaCl|(H_2)Pt} \tag{44}$$

which are expressed by the equation

$$E = \frac{RT}{F} \ln \frac{m_{H_3O^+} \cdot f_{H_3O^+}\,(\text{in HCl})}{m_{H_3O^+}{}' f_{H_3O^+}{}'\,(\text{in HA})} + \sum \varepsilon_{\text{diff.}} \qquad (45)$$

With the aid of an approximate value for the dissociation constant of HA, the ionic strengths in both half-cells can be made equal. Furthermore, if m_{HA} or $m_{HCl} \ll m_{NaCl}$, then the cell is largely symmetrical and therefore the sum of the diffusion potentials is almost equal to zero. Because of the equal ionic strengths on both sides, the equality $f_{H_3O^+} \simeq f_{H_3O^+}{}'$ is also probably true and hence from equation (45),

$$F = \frac{RT}{E} \ln \frac{m_{H_3O^+}}{m_{H_3O^+}{}'} \qquad (46)$$

If it is assumed that the hydrochloric acid is completely dissociated[25], $m_{H_3O^+}{}'$ and therefore $K_m{}'$ can be calculated. The latter is extrapolated to $I=0$ in the usual way. The provisions necessary for the approximate symmetry of the cell cause, however, a relatively large uncertainty in the measured values at those small ionic strengths which are especially important in the extrapolation of $\log K_m'$ to $\log K$, since this symmetry can be attained only approximately.

In the cell described by Owen[26]

$$\underset{}{\overset{\text{I}}{\text{Ag}|\text{AgCl}|\underset{mx}{\text{KCl}},\underset{m(1-x)}{\text{KNO}_3}|\underset{m}{\text{KNO}_3}|\underset{mx}{\text{AgNO}_3},\underset{m(1-x)}{\text{KNO}_3}}}\overset{\text{II}}{|\text{AgCl}|\text{Ag}} \qquad (47)$$

the extrapolation $x \to 0$ leads to complete symmetry and therefore to the elimination of the diffusion potential, $\sum \varepsilon_{\text{diff.}}$ By substituting the solubility product of AgCl

$$K = a_{Ag^+} \cdot a_{Cl^-}$$

into the expression for the E.M.F. of the cell

$$E = k \log \frac{a_{Ag^+}{}^{\text{II}}}{a_{Ag^+}{}^{\text{I}}} + \sum \varepsilon_{\text{diff.}}$$

the equations

$$E - k \log a_{Ag^+}{}^{\text{II}} a_{Cl^-}{}^{\text{I}} = -k \log K + \sum \varepsilon_{\text{diff.}}$$

$$E - 2k \log (mx) = -k \log K + k \log f_{Cl^-}{}^{\text{I}} f_{Ag^+}{}^{\text{II}} + \sum \varepsilon_{\text{diff.}} \qquad (48)$$

are obtained.

The extrapolation $x \to 0$ yields

$$[E - 2k \log (mx)]_{x=0} = k \log K + [k \log f_{Cl^-}{}^{\text{I}} f_{Ag^+}{}^{\text{II}}]_{x=0} \qquad (49)$$

The activity coefficient term in equation (49) is now thermodynamically defined in contrast to that in equation (48). Owing to the symmetry present in the cell at $x=0$, the indices I or II are superfluous. Extrapolation of the left hand side of equation (49) to $m=0$ gives $\log K$. The possibility of extrapolating equation (48) to $x=0$ rests on the non-thermodynamic basis already discussed. It is, however, so simple and plausible that no fundamental error is to be expected. The equality of the ionic strengths on both sides appears

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Für die E.M.K. dieser Zelle gilt

$$E = \frac{RT}{F} \ln \frac{m_{H_3O^+} f_{H_3O^+} \text{ (in HCl)}}{m_{H_3O^+}' f_{H_3O^+}' \text{ (in HA)}} + \sum \varepsilon_{\text{diff.}} \tag{45}$$

Mit Hilfe eines Näherungswertes für die Dissoziationskonstante von HA können die Ionenstärken auf beiden Seiten gleich gemacht werden. Wenn weiter m_{HA} bzw. $m_{HCl} \ll m_{NaCl}$ ist, so ist die Zelle weitgehend symmetrisch, und damit die Summe der Diffusionspotentiale praktisch gleich Null. Wegen der gleichen Ionenstärke auf beiden Seiten wird weiter gelten $f_{H_3O^+} \simeq f_{H_3O^+}'$, so daß aus Gleichung (45) wird

$$E = \frac{RT}{F} \ln \frac{m_{H_3O^+}}{m_{H_3O^+}'} \tag{46}$$

Unter der Annahme, daß die Salzsäure vollständig dissoziiert ist[25], läßt sich dann $m_{H_3O^+}'$ und damit K_m' berechnen. Letzteres wird in der mehrfach beschriebenen Art auf $\mathcal{J} = 0$ extrapoliert. Die zur angenäherten Symmetrie der Zelle notwendigen Voraussetzungen bedingen jedoch gerade bei den zur Extrapolation $\log K_m' \to \log K$ besonders wichtigen kleinen Ionenstärken eine relativ große Unsicherheit in den Meßwerten, die darin besteht, daß diese Symmetrie nur annähernd erreicht werden kann.

In der von Owen[26] beschriebenen Zelle

$$\underset{}{\overset{\text{I}}{\text{Ag}|\text{AgCl}|\underset{mx}{\text{KCl}},\underset{m(1-x)}{\text{KNO}_3}|\underset{m}{\text{KNO}_3}|\underset{mx}{\text{AgNO}_2},\underset{m(1-x)}{\text{KNO}_3}}}\overset{\text{II}}{|\text{AgCl}|\text{Ag}} \tag{47}$$

führt die Extrapolation $x \to 0$ zur völligen Symmetrie und damit zum Verschwinden der Diffusionspotentiale $\sum \varepsilon_{\text{diff.}}$ Durch Kombination der Löslichkeitskonstante von AgCl

$$K = a_{Ag^+} a_{Cl^-}$$

mit

$$E = k \log \frac{a_{Ag^+}^{II}}{a_{Ag^+}^{I}} + \sum \varepsilon_{\text{diff.}}$$

ergibt sich

$$E - k \log a_{Ag^+}^{II} a_{Cl^-}^{I} = -k \log K + \sum \varepsilon_{\text{diff.}}$$

$$E - 2k \log (mx) = -k \log K + k \log f_{Cl^-}^{I} f_{Ag^+}^{II} + \sum \varepsilon_{\text{diff.}} \tag{48}$$

Die Extrapolation $x \to 0$ ergibt

$$[E - 2k \log (mx)]_{x=0} = k \log K + [k \log f_{Cl^-}^{I} f_{Ag^+}^{II}]_{x=0} \tag{49}$$

Der Aktivitätskoeffiziententerm in Gl. (49) ist jetzt im Gegensatz zu dem in Gl. (48) thermodynamisch definiert. Wegen der bei $x = 0$ vorliegenden Symmetrie der Zelle sind die Indices I bzw. II überflüssig. Die Extrapolation der Ausdrücke in (49) auf $m = 0$ führt zu $\log K$. Die Möglichkeit, Gl. (48) auf $x = 0$ zu extrapolieren, ist der nichtthermodynamische Ansatz, der hier gemacht wurde. Er ist indessen so einfach und plausibel, daß hieraus keine prinzipiellen Fehler zu erwarten sind. Wesentlich dafür, daß

to be essential if this extrapolation is to be linear and therefore sufficiently exact[27]. For weak electrolytes, this stipulation is not satisfied unless the K_c^- to be determined is approximately known or unless a tedious successive approximation procedure is used.

Finally, the differential potentiometric method[28] must be discussed. The K_c^- values obtained in this way depend only slightly on the diffusion potential present, and on the standard E.M.F. of the cell, if cells without diffusion potentials are employed. Therefore it is not essential, for example, that $\sum \varepsilon_{diff.}$ should disappear, but only that it should be constant for the addition of small amounts of acids or bases. The course of the pH in the titration of a weak acid with a strong base depends on the initial concentrations and, above all, on the strength of the acid. The classical dissociation constants of acids can be determined from the slope of the titration curve if several assumptions are made (see below). According to Kilpi[29], the approximate equation

$$P = 4{\cdot}606\sqrt{K_c^- c}\left(1 - \sqrt{\frac{K_c^-}{c}} - \frac{1}{2}\cdot\frac{K_c^-}{c} + \ldots\right) \tag{50}$$

is valid, for example, at the point of inflection. In this equation, c is the stoichiometric concentration of the acid at the point of inflection; $P = \mathrm{d}c_B/\mathrm{dpH}_{(c)}$ is the corresponding buffering capacity; c_B is the stoichiometric concentration of the base added at the point of inflection; and $\mathrm{pH}_{(c)} = -\log c_{H_3O^+}$. The calculation requires the following assumptions.

(1) K_c^- is independent of concentration in the range in which P is determined.

(2) Conventional pH′ values, which have been established by measurements in cells of type (36), can be used instead of $\mathrm{pH}_{(c)}$ in $P = \mathrm{d}c_B/\mathrm{dpH}_{(c)}$.

(3) The diffusion potentials in cell (36) are constant within the range in which P is measured.

These assumptions can only be verified approximately. They are more likely to be true, the smaller the amount of base which is required to establish the particular value of P. The accuracy attained is limited for this reason and no further general statement can be made about it. The accuracy therefore depends essentially on how precisely the smallest possible alterations in the pH can be measured.

4. DETERMINATION OF DISSOCIATION CONSTANTS BY CATALYTIC MEASUREMENTS[30]

A group of chemical reactions are catalysed by proton acceptors or donors, i.e. by acids or bases in the Brönsted sense[31]. Usually, with regard to the reactants, a first-order reaction is involved, for which (as a first approximation) the expression

$$-\frac{\mathrm{d}c_A}{\mathrm{d}t} = kc_A \tag{51}$$

is valid. The rate constant k is proportional to the concentration of the catalytically active material i:

$$k = k_0 + \sum k_i c_i \tag{52}$$

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diese Extrapolation linear verläuft und damit genau genug ist, scheint die Gleichheit der Ionenstärke auf beiden Seiten zu sein[27]. Bei schwachen Elektrolyten ist diese Bedingung ohne Kenntnis des zu ermittelnden K nicht oder nur durch ein mühsames experimentelles Näherungsverfahren zu erreichen.

Zum Schluß seien noch die differential-potentiometrischen Verfahren[28] besprochen. Die damit erhaltenen K_c-Werte hängen nur wenig von vorhandenen Diffusionspotentialen ab, bzw. von der Standard-E.M.K. der Zelle, wenn mit Zellen ohne Diffusionspotential gearbeitet wird. Das kommt daher, daß z.B. nicht gefordert wird, daß $\sum \varepsilon_{\text{diff.}}$ verschwindet, sondern nur, daß es bei Zufügung kleiner Säure- oder Basenmengen konstant sein soll. Der pH-Verlauf bei der Titration einer schwachen Säure mit einer starken Base hängt außer von der Ausgangskonzentration vor allem von der Stärke der Säure ab. Aus der Steigung der Titrationskurve kann mit einigen Annahmen (siehe unten) die klassische Dissoziationskonstante der Säure bestimmt werden. Nach Kilpi[29] gilt z.B. für den Wendepunkt die Näherungsgleichung

$$P = 4{,}606\sqrt{K_c c}\left(1 - \sqrt{\frac{K_c}{c}} - \frac{1}{2}\cdot\frac{K_c}{c} + \dots\right). \tag{50}$$

Darin bedeuten: c die stöchiometrische Säurekonzentration am Wendepunkt; $P = \mathrm{d}c_B/\mathrm{dpH}_{(c)}$ die Pufferkapazität; c_B die stöchiometrische Konzentration der zugefügten Base am Wendepunkt; $\mathrm{pH}_{(c)} = -\log c_{H_3O^+}$. Die Rechnung benützt folgende Annahmen:

(1) K_c ist in dem Bereich, in dem P bestimmt wird, konzentrationsunabhängig;

(2) statt $\mathrm{pH}_{(c)}$ kann in $P = \mathrm{d}c_B/\mathrm{dpH}_{(c)}$ der aus Messungen an Zellen des Typs (36) ermittelte konventionelle pH'-Wert verwendet werden;

(3) die Diffusionspotentiale in Zelle (36) sollen innerhalb des Bereichs, in dem P gemessen wird, konstant sein.

Diese Annahmen können nur angenähert verifiziert werden. Sie werden umso besser erfüllt sein, je kleinere Basenmengen zur Ermittlung von P zugesetzt werden. Aus diesem Grund ist die erzielbare Genauigkeit begrenzt. Allgemein läßt sich darüber nichts aussagen. Sie wird wesentlich davon abhängen, wie genau möglichst kleine Änderungen des pH gemessen werden können.

4. BESTIMMUNG DER DISSOZIATIONSKONSTANTEN AUS KATALYTISCHEN MESSUNGEN[30]

Eine Gruppe chemischer Reaktionen wird durch Protonenakzeptoren bzw. -donatoren, d.h. durch Basen bzw. Säuren im Brönsted'schen Sinne[31] katalysiert. Meistens handelt es sich dabei im Hinblick auf die reagierenden Stoffe um Reaktionen erster Ordnung, für die (in erster Näherung) gilt

$$-\frac{\mathrm{d}c_A}{\mathrm{d}t} = kc_A \tag{51}$$

Hierbei ist die Geschwindigkeitskonstante k proportional den Konzentrationen der katalytisch wirksamen Stoffe i:

$$k = k_0 + \sum k_i c_i \tag{52}$$

k_0 ist die Konstante der spontan ablaufenden Reaktion.

where k_0 is the rate constant of the spontaneous or uncatalysed reaction.

The situation for acid catalysis only is described below, but that for base catalysis is wholly analogous. For the determination of the hydrogen ion concentration, the most favourable case occurs when only the H_3O^+ ions are catalytically active:

$$k = k_0 + k_{H_3O^+} c_{H_3O^+} \tag{53}$$

In this case, measurements of k with a strong acid as catalyst ($c_{H_3O^+} = c_{acid}$) permit the determination of $k_{H_3O^+}$. If the measurements are repeated with a weak acid, $c_{H_3O^+}$ is immediately derivable[32]. However, equation (53) is usually an insufficient description of the results in the case of catalysis by weak acids. Although the action of the anion can often be neglected[33], the undissociated acid is usually also catalytically active[34]. The equation must then be modified to

$$k = k_0 + k_{H_3O^+} c_{H_3O^+} + k_{HA} c_{HA} \tag{54}$$

where k_{HA} can be determined in solutions containing a buffer mixture of HA and, e.g., NaA, for c_{HA} can then be varied with approximately constant $c_{H_3O^+}$. In such cases this procedure can also lead to a determination[35] of $c_{H_3O^+}$. But any catalytic action of the undissociated acid is superimposed on the so-called salt effect: the k_i in equation (52) depends on the ionic strength I (primary salt effect)[36], and, moreover, the dissociation of the weak acid is affected by the ionic strength (secondary salt effect)[37]. The necessity of eliminating these salt effects causes an additional uncertainty in the determination of k_{HA}. For this reason, the dissociation constants which are determined by catalytic measurements are mostly of qualitative significance only. Further difficulties lie in the exact determination of any autocatalysis[38] if the reaction products are themselves acids. Finally, it should also be noted that the presence of the reactants alters the properties of the solvent, so that these K values are only approximately equal to those obtained in pure solvents.

5. DETERMINATION OF DISSOCIATION CONSTANTS BY OPTICAL METHODS

In general, the optical properties of an undissociated acid HA are different from those of its anion A^-. This is true, for example, for the refraction, the fluorescence, the Raman effect, the light absorption, etc. If it is possible to make use of this difference for the determination of the concentrations of the two forms HA and A^-, then the dissociation constants can be calculated.

The most exact K values are obtained from the different absorption characteristics[39] of HA and A^-. Direct measurements of the degree of dissociation require the preliminary assumption that a wavelength is available at which the extinction coefficient of one form is negligible in comparison with that of the other; alternatively that the extinction coefficients are very different, e.g. $\varepsilon_{HA} \ll \varepsilon_{A^-}$. If K is not very small, almost no free acid is present in a weakly alkaline solution of the sodium salt of the acid. Measurements of the extinction of such solutions then lead to ε_{A^-} and hence to the determination of α in solutions containing different concentrations of the pure

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Im folgenden sollen nur die Verhältnisse bei einer Säurekatalyse beschrieben werden, da für die Basenkatalyse Analoges gilt. Zur Bestimmung der Wasserstoffionenkonzentration wäre der günstigste Fall der, daß nur die H_3O^+ Ionen katalytisch wirken:

$$k = k_0 + k_{H_3O} \cdot c_{H_3O^+} \tag{53}$$

In diesem Fall erlauben Messungen von k mit einer starken Säure als Katalysator ($c_{H_3O^+} = c_{Säure}$) die Bestimmung von $k_{H_3O^+}$. Werden die Messungen mit einer schwachen Säure wiederholt, so ist $c_{H_3O^+}$ sofort zugänglich[32]. Nun genügt Gl. (53) gerade im Falle der Katalyse durch schwache Säuren meistens nicht zur Beschreibung der Meßergebnisse. Wenn auch die Wirkung des Anions oft zu vernachlässigen ist[33], so wirkt die undissoziierte Säure meistens ebenfalls katalytisch[34]. Es gilt dann

$$k = k_0 + k_{H_3O} \cdot c_{H_3O^+} + k_{HA} c_{HA} \tag{54}$$

k_{HA} kann bestimmt werden an Lösungen aus Puffergemischen aus HA und z.B. NaA, denn dann kann c_{HA} bei angenähert konstantem $c_{H_3O^+}$ variiert werden. Auf diese Weise kann man auch in solchen Fällen zu einer Bestimmung von $c_{H_3O^+}$ gelangen[35]. Nun überlagern sich einer evtl. vorhandenen katalytischen Wirkung der undissoziierten Säure die sog. Salzeffekte: Die k_i in Gl. (52) hängen von der Ionenstärke $\mathcal{J}$ ab (primärer Salzeffekt)[36], außerdem wird die Dissoziation der schwachen Säure durch die Ionenstärke beeinflußt (sekundärer Salzeffekt)[37]. Die Notwendigkeit, diese Salzeffekte zu eliminieren, bedingt eine zusätzliche Unsicherheit in der Bestimmung von k_{HA}. Deswegen sind die Dissoziationskonstanten, die aus katalytischen Messungen ermittelt werden, meistens nur von orientierendem Wert. Weitere Schwierigkeiten liegen in der exakten Ermittlung einer evtl. vorhandenen Autokatalyse[38], wenn die Reaktionsprodukte selbst Säuren sind. Schließlich muß auch beachtet werden, daß die Gegenwart der reagierenden Stoffe die Eigenschaften des Lösungsmittels verändern, so daß diese K-Werte nur angenähert gleich denen im reinen Lösungsmittel sind.

5. BESTIMMUNG DER DISSOZIATIONSKONSTANTEN MIT OPTISCHEN METHODEN

Gewöhnlich unterscheiden sich die optischen Eigenschaften einer undissoziierten Säure HA von denen ihres Anions A^-. Das gilt z.B. für die Refraktion, die Fluoreszenz, den Ramaneffekt, die Lichtabsorption etc. Wenn es gelingt, diese Unterschiede zu Konzentrationsbestimmungen der beiden Formen HA und A^- heranzuziehen, so können daraus Dissoziationskonstanten berechnet werden.

Die genauesten K-Werte sind aus dem verschiedenen Absorptionsvermögen von A^- und HA zugänglich[39]. Für direkte Messungen des Dissoziationsgrades muß zunächst die Voraussetzung erfüllt sein, daß es eine Wellenlänge gibt, bei der der Extinktionskoeffizient der einen Form gegen den der anderen vernachlässigt werden kann, bzw. bei der beide sehr verschieden sind, z.B. $\varepsilon_{HA} \ll \varepsilon_{A^-}$. Wenn K nicht sehr klein ist, wird in einer schwach alkalischen Lösung des Natriumsalzes der Säure praktisch keine

acid. The K_c' values calculated from α are extrapolated to $I=0$ in the usual way. The method only requires the assumption that ε_{A^-} is independent of the cation (Na^+ or H_3O^+ ions) at the concentrations involved. From measurements in salt solutions containing different cations, the correctness of this assumption cannot be put higher than probable. The applicability of the method to precise determinations of K_c' is therefore restricted to ranges of concentrations in which specific differences in the ionic effect on ε_{A^-} are not to be expected[40], i.e. at ionic concentrations of less than 10^{-2}. On the other hand, the method possesses two real advantages. First, the true dissociation constants can be measured directly without interionic effects having to be considered. The optical properties of the ions are virtually constant up to relatively high concentrations[40]. Secondly, the measurements can be made at very small concentrations with the same relative accuracy as at high concentrations (by increasing the thickness of the layer). Extrapolation of K_c' to K' is therefore more certain than, for example, in the electrometric methods. Absorption measurements of this type yield very reliable K' values in favourable cases. In less favourable circumstances, when there is no wavelength where $\varepsilon_{HA} \ll \varepsilon_{A^-}$, approximation methods can lead to relatively reliable values, provided that ε_{HA} is sufficiently different from ε_{A^-}. With very small values of K_c', the hydrolysis

$$A^- + H_2O \rightleftharpoons HA + OH^- \tag{55}$$

cannot be ignored even in alkaline salt solutions. The constant K_h' of the hydrolysis,

$$K_h' = \frac{[c_{A^-}]}{[c_{HA}][c_{OH^-}]} \cdot \frac{f_{A^-}}{f_{HA} f_{OH^-}} \tag{56}$$

can then be determined together with ε_{A^-} by an extrapolation procedure[42]. If the ionic concentration is small enough, the activity coefficients of the negative ions are practically equal to each other, and hence

$$K_h' \simeq \frac{[c_{A^-}]}{[c_{HA}][c_{OH^-}]} \tag{56a}$$

If an apparent extinction coefficient ε' is defined by

$$\varepsilon' d(c_{A^-} + c_{HA}) = \log \frac{\Phi_0}{\Phi} \equiv E \tag{57}$$

and further if $\varepsilon_{HA} \ll \varepsilon_{A^-}$, a simple calculation gives

$$\frac{1}{\varepsilon'} = \frac{1}{\varepsilon} + \frac{1}{c_{OH^-}} \cdot \frac{1}{\varepsilon_{A^-} K_h'}. \tag{58}$$

Values of ε' are determined for solutions containing different concentrations of hydroxyl ion ($c_{OH^-} \gg c_{acid}$) and extrapolated according to equation (58). The K_h' thus obtained can be converted into the K' value of the acid by means of the known ionic product of water. This extrapolation causes some uncertainties, for it must be made from relatively large values of $1/c_{OH^-}$ down to $1/c_{OH^-} = 0$; at small values of $1/c_{OH^-}$, ε_{A^-} is no longer constant and, besides, equation

freie Säure mehr vorliegen. Extinktionsmessungen an solchen Lösungen führen dann zu ε_{A^-} und damit zur Ermittlung von α in Lösungen der reinen Säure verschiedener Konzentration. Die aus α berechneten K_c-Werte werden in üblicher Weise auf $J=0$ extrapoliert. In dem Verfahren steckt nur die eine Annahme, daß ε_{A^-} bei den verwendeten Konzentrationen unabhängig ist vom Kation (Na^+ bzw. H_3O^+-Ion). Die Richtigkeit dieser Annahme kann durch Messungen an Salzlösungen mit verschiedenem Kation nur wahrscheinlich gemacht werden. Dieser Umstand schränkt die Anwendbarkeit der Methode für Präzisionsbestimmungen von K_c auf Konzentrationsgebiete ein, für die spezifische Unterschiede in der Ionenwirkung auf ε_{A^-} nicht zu erwarten sind[40], d.h. auf Ionenkonzentrationen $J<10^{-2}$. Demgegenüber weist die Methode zwei wesentliche Vorzüge auf: Einmal können so direkt wahre Dissoziationsgrade gemessen werden, ohne daß die interionische Wechselwirkung berücksichtigt werden muß. Die optischen Eigenschaften der Ionen dagegen sind bis zu relativ hohen Konzentrationen praktisch konstant[40]. Zweitens kann auch bei sehr kleinen Konzentrationen noch mit gleicher relativer Sicherheit gemessen werden, wie bei höheren (durch Vergrößerung der Schichtdicke). Daher ist die Extrapolation der K_c auf K sicherer als z.B. bei elektrometrischen Verfahren. Derartige Absorptionsmessungen liefern in günstigen Fällen sehr sichere K-Werte. In den weniger günstigen Fällen, wo bei keiner Wellenlänge $\varepsilon_{HA} \ll \varepsilon_{A^-}$, können Näherungsverfahren zu relativ sicheren Werten führen, wenn ε_{HA} genügend verschieden von ε_{A^-} ist[41]. Bei sehr kleinen K_c-Werten kann auch in alkalischen Salzlösungen die Hydrolyse

$$A^- + H_2O \rightleftharpoons HA + OH^- \tag{55}$$

nicht vernachlässigt werden. Die Konstante K_h der Hydrolyse

$$K_h = \frac{[c_{A^-}]}{[c_{HA}][c_{OH^-}]} \cdot \frac{f_{A^-}}{f_{HA} f_{OH^-}} \tag{56}$$

kann nun zusammen mit ε_{A^-} durch ein Extrapolationsverfahren[42] bestimmt werden. Bei genügend kleinen Ionenkonzentrationen werden die Aktivitätskoeffizienten der negativen Ionen einander praktisch gleich, so daß

$$K_h \simeq \frac{[c_{A^-}]}{[c_{HA}][c_{OH^-}]} \tag{56a}$$

Wenn nun ein scheinbarer Extinktionskoeffizient ε' definiert wird durch

$$\varepsilon' d(c_{A^-} + c_{HA}) = \log \frac{\Phi_0}{\Phi} \equiv E \tag{57}$$

und weiter $\varepsilon_{HA} \ll \varepsilon_{A^-}$, so führt eine einfache Rechnung zu

$$\frac{1}{\varepsilon'} = \frac{1}{\varepsilon} + \frac{1}{c_{OH^-}} \cdot \frac{1}{\varepsilon_{A^-} K_h} \tag{58}$$

Man bestimmt ε' für Lösungen verschiedener OH^--Konzentration ($c_{OH^-} \gg c_{Säure}$) und extrapoliert nach Gl. (58). Das so erhaltene K_h kann mit dem bekannten Ionenprodukt des Wassers in K der Säure umgerechnet werden. Diese Extrapolation bedingt einige Unsicherheiten, denn es muß von relativ

(36a) is not valid. Nevertheless, K' values determined in this way are quite reliable, considering the difficulties of determining very small values of K'.

With large K' values, a limit is often imposed by the accuracy with which the measurements can be extended to small concentrations[43]. This happens when the absorption of the dissociated part only can be measured, because the relative error

$$\frac{dK'_c}{K'_c} = \frac{2-\alpha}{1-\alpha} \cdot \frac{d\alpha}{\alpha} \tag{59}$$

is then very large.

Another procedure combines the electrometric and absorptiometric measurements[44]. First, the ratio c_A^- / c_{HA} of the weak acid in a solution of a strong acid (e.g. HCl, $c_{HCl} > c_{HA}$) is determined optically. In addition, the expression $a_{H_3O^+} \cdot f_{Cl^-}$ is determined electrometrically on the same solution in a cell without a diffusion potential[45], e.g.

$$Pt(H_2)|Solution,\ Cl^-|AgCl|Ag$$

The cell gives first $\log a_{H_3O^+} \cdot a_{Cl^-}$; the product $a_{H_3O^+} f_{Cl^-}$ can then be computed from the known value of c_{Cl^-} ($= c_{HCl}$). When

$$pK' \equiv -\log a_{H_3O^+} f_{Cl^-} - \log \frac{c_A^-}{c_{HA}}$$

is plotted against I, it shows an essentially smaller dependence on I than pK'_c, as can readily be seen from the equations

$$pK' = -\log a_{H_3O^+} f_{Cl^-} - \log \frac{c_{A^-}}{c_{HA}}$$

and

$$pK' = -\log a_{H_3O^+} f_{A^-} - \log \frac{c_A^-}{c_{HA}}$$

But when $I = 0$, $pK' = pK'$. Actually, it is only necessary to extrapolate as far as an I value where no further individual differences occur in the activity coefficients, and where, therefore, pK' is already equal to pK'. The reliability of the K' values obtained therefore depends on whether pK' varies linearly with I. Extrapolation is only certain in these cases, because relatively large uncertainties can be introduced by errors in the measurement of the E.M.F. at very small concentrations.

In the solution of a weak acid, HA, which also contains an indicator acid, HIn, the dissociation equilibrium of both acids is governed by the hydrogen ion activity. Various procedures can be followed for the determination of the dissociation constants of HA from the ratio c_{In^-} / c_{HIn}. One method[46] consists of calculating first the ratio

$$\frac{K'_{c_{HIn}}}{K'_{c_{HA}}} = \frac{[c_{In^-}][c_{HA}]}{[c_{HIn}][c_{A^-}]} \tag{60}$$

Measurements in solutions of the indicator acid in a buffer mixture of HA and NaA are necessary for this purpose. If the hydrogen ion concentration

großen Werten für $1/c_{OH^-}$ hier auf $1/c_{OH^-}=0$ extrapoliert werden, weil bei kleinen $1/c_{OH^-}$ das ε_{A^-} nicht mehr konstant ist, und außerdem Gl. (56a) ungültig wird. Immerhin kommt den so bestimmten K-Werten eine, gemessen an den Schwierigkeiten in der Bestimmung sehr kleiner K-Werte, relativ große Zuverlässigkeit zu.

Bei großem K setzt die Meßgenauigkeit der Ausdehnung der Messungen auf kleinste Konzentrationen oft eine Grenze[43]. Das tritt dann ein, wenn nur die Absorption des dissoziierten Anteils gemessen werden kann, weil dann der relative Fehler

$$\frac{\mathrm{d}K_c}{K_c} = \frac{2-\alpha}{1-\alpha}\cdot\frac{\mathrm{d}\alpha}{\alpha} \tag{59}$$

sehr groß wird.

Ein anderes Verfahren verknüpft elektrometrische mit Absorptionsmessungen[44]. Danach wird einmal das Verhältnis c_{A^-}/c_{HA} der schwachen Säure in einer Lösung einer starken Säure (z.B. HCl, $c_{HCl}>c_{HA}$) optisch bestimmt. Zusätzlich wird der Ausdruck $a_{H_3O^+}\cdot f_{Cl^-}$ der gleichen Lösung elektrometrisch mit einer Zelle ohne Diffusionspotential

$$\mathrm{Pt(H_2)|Lösung,\ Cl^-|AgCl|Ag}$$

bestimmt.[45] Die Zelle liefert zunächst $\log a_{H_3O^+}\cdot a_{Cl^-}$. Mit c_{Cl^-} $(=c_{HCl})$ kann $a_{H_3O^+}\cdot f_{Cl^-}$ berechnet werden.

$$\mathrm{p}K' \equiv -\log a_{H_3O^+}\cdot f_{Cl^-} - \log\frac{c_{A^-}}{c_{HA}}$$

gegen $\bar{\jmath}$ aufgetragen, zeigt eine wesentlich geringere Abhängigkeit von $\bar{\jmath}$ als $\mathrm{p}K_c$, wie man aus dem Vergleich von

$$\mathrm{p}K' = -\log a_{H_3O^+}\cdot f_{Cl^-} - \log\frac{c_{A^-}}{c_{HA}}$$

$$\mathrm{p}K = -\log a_{H_3O^+}\cdot f_{A^-} - \log\frac{c_{A^-}}{c_{HA}}$$

sofort ersieht. Für $\bar{\jmath}=0$ wird aber $\mathrm{p}K'=\mathrm{p}K$. Die Extrapolation braucht eigentlich nur bis zu einem $\bar{\jmath}$ vorgenommen zu werden, wo keine individuellen Unterschiede in den Aktivitätskoeffizienten mehr auftreten, und deshalb bereits $\mathrm{p}K'=\mathrm{p}K$ wird. Die Zuverlässigkeit der so gewonnenen K wird davon abhängen, ob $\mathrm{p}K'$ linear mit $\bar{\jmath}$ variiert. Nur in diesem Falle wird die Extrapolation sicher sein, da wegen der Meßfehler der E.M.K.-Messungen bei sehr kleinen Konzentrationen relativ große Unsicherheiten auftreten.

In der Lösung einer schwachen Säure HA, die gleichzeitig eine Indikatorsäure HIn enthält, sind die Dissoziationsgleichgewichte beider Säuren über die Wasserstoffionenaktivität gekoppelt. Für die Bestimmung der Dissoziationskonstanten von HA aus dem Verhältnis c_{In^-}/c_{HIn} können verschiedene Wege eingeschlagen werden. Die eine Methode[46] besteht darin, zunächst das Verhältnis

$$\frac{K_{c_{HIn}}}{K_{c_{HA}}} = \frac{[c_{In^-}][c_{HA}]}{[c_{HIn}][c_{A^-}]} \tag{60}$$

zu berechnen. Dazu sind Messungen an Lösungen der Indikatorsäure in

is known, so that a correction for the hydrolysis can be applied, the term c_{HA}/c_{A^-} can be calculated from the composition of the buffer mixture. $c_{H_3O^+}$ is calculated from c_{HIn}/c_{In^-} and the K_c' value of the indicator. An approximation is necessary because the ionic strength is not known exactly if the hydrogen ion concentration is unknown. This is particularly true if pure solutions of acids are used instead of buffer solutions[47]. The expression (60) obtained in this way can usually be extrapolated to $I=0$ with certainty, for it only differs from the ratio of the thermodynamic constants by the ratio of the individual variations of the activity coefficients. This latter ratio is obtained from the Debye-Hückel limiting law. If K' of the indicator is known, K'_{HA} can be obtained directly, and thus the method assumes previous knowledge of the K' value of the indicator. The dependence of ε_{In^-} on the ionic strength and on the concentration of the free acid must be given especial attention, for the buffer substance is still present along with the ions which are determined optically. In all cases where $f_\pm$ as well as ε_{A^-} is dependent on the concentration, different functions $K'_{HIn}/K'_{HA}=f(I)$ are obtained if the buffer ratio c_{HA}/c_{A^-} is varied. But all such functions still yield the same limiting value for $I=0$. The accuracy of the extrapolation must be considered in each individual case.

In another variation of the method, the hydrogen ion concentration or activity is calculated from c_{HIn}/c_{In^-}. This is done either from the (known) K_c' of the indicator or by calibration of the indicator with buffer solutions of known pH[48].

K_c' or $K'=a_{H_3O^+}\dfrac{c_A}{c_{HA}}$ for the acid HA can be calculated from $c_{H_3O^+}$ or $a_{H_3O^+}$. The extrapolation of both expressions to $I=0$ yields K'. It should obviously be obtained from measurements within the Debye-Hückel range down to the smallest possible concentrations. For the calibrations with buffer solutions, it should be noted that it is not the ratio of the concentrations but that of the activities of the two indicator forms which depends on the pH. The ionic strengths must be the same for the calibration and for the actual measurements. It should also be noted for this method that the pH values of the buffer solutions employed for the calibration are usually the conventional values. Only approximate values for K' are then obtained.

The K_c' values of the indicators as a function of the ionic strength are known with the necessary certainty in only a very few cases. The K_c' values of the acids which are determined by this means are therefore no more accurate than the K_c' value of the indicator. However, it is possible to manage without any knowledge of the K_c' of the indicator acid[49]. The solutions of the acid being studied and indicator are compared with similar solutions containing the same concentration of the indicator and also the appropriate concentration of a strong mineral acid (e.g. HCl) required for the extinction coefficients of the test and comparison solutions to be the same. The expressions

$$c_{H_3O^+} = c_{HCl} + c_{In^-} \quad c_{A^-} = c_{HCl}$$

$$K_c' = \frac{[c_{HCl}][c_{HCl}+c_{In^-}]}{[c_{HA}-c_{HCl}]}$$

einem Puffergemisch von HA und NaA nötig. Bei Kenntnis der Wasserstoffionenkonzentration zur Korrektur für die Hydrolyse kann aus der Zusammensetzung des Puffergemisches der Ausdruck c_{HA}/c_{A^-} berechnet werden. $c_{H_3O^+}$ wird aus c_{HIn}/c_{In^-} und K_c des Indikators berechnet. Hierbei ist eine Näherung notwendig, da bei unbekannter Wasserstoffionenkonzentration die Ionenstärke nicht genau bekannt ist. Das gilt besonders dann, wenn statt mit Pufferlösungen mit reinen Säurelösungen gearbeitet wird[47]. Der so erhaltene Ausdruck (60) läßt sich meistens sicher auf $\mathcal{J}=0$ extrapolieren, weil er sich nur durch das Verhältnis der individuellen Abweichungen der Aktivitätskoeffizienten vom Verhältnis der thermodynamischen Konstanten unterscheidet. Letzteren Wert nimmt er beim Erreichen des Debye–Hückel-Grenzgebietes an. Bei Kenntnis von K des Indikator ist K_{HA} sofort anzugeben. Das Verfahren setzt die Kenntnis von K des Indikators voraus. Der Abhängigkeit von ε_{In^-} von der Ionenstärke und den Konzentrationen der freien Säuren ist hier besondere Aufmerksamkeit zu widmen, da neben dem optisch bestimmbaren Ion noch die Puffersubstanzen vorliegen. In allen Fällen, wo außer den $f_\pm$ auch ε_{A^-} von der Konzentration abhängt, werden verschiedene Funktionen $(K_{HIn}/K_{HA})=f(\mathcal{J})$ erhalten, wenn das Pufferverhältnis c_{HA}/c_{A^-} variiert wird. Doch liefern alle derartigen Funktionen den gleichen Grenzwert für $\mathcal{J}=0$. Die Genauigkeit der Extrapolation muß in jedem einzelnen Falle diskutiert werden.

Bei anderen Varianten der Methode wird aus c_{HIn}/c_{In^-} die Wasserstoffionenkonzentration bzw. -aktivität berechnet. Das geschieht entweder mit dem (bekannten) K_c des Indikators oder durch Eichung des Indikators mit Pufferlösungen von bekanntem pH[48].

Aus $c_{H_3O^+}$ bzw. $a_{H_3O^+}$ kann K_c bzw. $K'=a_{H_3O^+}\dfrac{c_{A^-}}{c_{HA}}$ für die Säure HA berechnet werden. Die Extrapolation beider Ausdrücke auf $\mathcal{J}=0$ liefert K. Hier kommt es offenbar auf Messungen innerhalb des Debye–Hückel-Gebietes bis hinunter zu möglichst kleinen Konzentrationen an. Bei Eichungen mit Pufferlösungen ist zu beachten, daß nicht das Verhältnis der Konzentrationen der beiden Indikatorformen vom pH abhängt, sondern das Aktivitätsverhältnis. Es ist also notwendig, daß die Ionenstärke bei der Eichung und bei der Messung die gleiche ist. Weiter ist bei dieser Methode zu beachten, daß die pH-Werte der zur Eichung verwendeten Pufferlösungen meistens konventionelle Werte sind. Man erhält dann nur Näherungswerte für die K.

Die K_c-Werte der Indikatoren als Funktion der Ionenstärke sind nur in den wenigsten Fällen mit der nötigen Sicherheit bekannt. Die mit ihrer Hilfe bestimmten K_c der untersuchten Säure sind nicht genauer als letztere. Es gibt indessen eine Möglichkeit, ohne Kenntnis von K_c der Indikatorsäure auszukommen[49]. Man vergleicht die Lösungen der untersuchten Säure + Indikator mit einer solchen, die den Indikator in gleicher Konzentration enthält und ferner soviel einer starken Mineralsäure (z.B. HCl), daß die Extinktionen in Test- und Vergleichslösung gleich sind. Dann gilt

$$c_{H_3O^+} = c_{HCl} + c_{In^-} \quad c_{A^-} = c_{HCl}$$

$$K_c = \frac{[c_{HCl}][c_{HCl}+c_{In^-}]}{[c_{HA}-c_{HCl}]}$$

are then valid; c_{In^-} is determined by comparison with an alkaline indicator solution. If the acid under investigation is much stronger than the indicator acid, c_{In^-} corresponds only to a small correction. This method thus does not require knowledge of the K_c^* value of the indicator.

6. POLYBASIC ACIDS AND ZWITTER-IONS

In principle (with the use of acid salts) the same methods can be employed for the determination of the dissociation constants of *polybasic acids* as for those of monobasic acids, provided that the ratio K_1^*/K_2^* is of the order of 10^3 or more[50]. However, additional complications arise if this ratio falls below 10^3 so that the dissociations of the different stages overlap appreciably. Reliable values for the individual constants can be estimated successfully in such cases by the application of suitable extrapolation procedures, with the aid of the Debye–Hückel equation, to measurements made in cells without diffusion potentials of the type (28) or (33)[51].

The dissociation of amino acids was initially described by the simple equations

$$H_2N{\cdot}R{\cdot}COOH + H_2O \rightleftharpoons H_2N{\cdot}R{\cdot}COO^- + H_3O^+ \; ; \; K_{acid}^* = \frac{[a_R\,][a_{H_3O^+}]}{[a_R]} \tag{61}$$

and

$$H_2N{\cdot}R{\cdot}COOH + H_2O \rightleftharpoons H_3\overset{+}{N}{\cdot}R{\cdot}COOH + OH^- \; ; \; K_{base}^* = \frac{[a_R\,][a_{OH^-}]}{[a_R]} \tag{62}$$

However, amino acids are more fundamentally regarded as *zwitter-ions*, i.e as internal salts, and involve a tautomeric equilibrium[52]. Consequently, in recent years, they have been described as dibasic acids (cationic acids) and their dissociation is formulated in the following way:

$$H_3\overset{+}{N}{\cdot}R{\cdot}COOH + H_2O \rightleftharpoons H_3\overset{+}{N}{\cdot}R{\cdot}COO^- + H_3O^+ \; ; \; K_1^* = \frac{[a_R\,]]a_{H_3O^+}]}{[a_R\,]} \tag{63}$$

and

$$H_3\overset{+}{N}{\cdot}R{\cdot}COO^- + H_2O \rightleftharpoons H_2N{\cdot}R{\cdot}COO^- + H_3O^+ \; ; \; K_2^* = \frac{[a_R{}^-][a_{H_3O^+}]}{[a_R\,]} \tag{64}$$

A comparison of the constants defined in this way shows that

$$K_2^* \equiv K_{acid}^* \quad \text{and} \quad K_1^* \equiv \frac{K_w^*}{K_{base}^*} \tag{65}$$

where K_w^* is the ionic product* of water,

$$K_w^* \equiv [a_{H_3O^+}][a_{OH^-}] \tag{66}$$

In the Tables, the values of K_1^* and K_2^* calculated[53] by means of K_w^* are always given.

* Represented by P in the German version.

c_{In^-} wird durch Vergleich mit einer alkalischen Indikatorlösung bestimmt. Wenn die untersuchte Säure viel stärker ist als die Indikatorsäure, so ist c_{In^-} nur eine kleine Korrekturgröße. Dieses Verfahren setzt also nicht die Kenntnis von K_i der Indikatorsäure voraus.

6. MEHRBASISCHE SÄUREN UND ZWITTERIONEN

Zur Bestimmung der Dissoziationskonstanten *mehrbasischer Säuren* kann man prinzipiell (unter Verwendung der sauren Salze) die gleichen Methoden benutzen, wie für die Bestimmung einbasischer Säuren, sofern das Verhältnis K_1/K_2 von der Größenordnung 10^3 oder größer ist[50]. Dagegen treten zusätzliche Komplikationen auf, wenn dieses Verhältnis wesentlich unter 10^3 sinkt, die Dissoziationen der verschiedenen Stufen sich also merklich überlappen. Durch Verwendung geeigneter Extrapolationsverfahren mit Hilfe der Debye-Hückel-Gleichung gelingt es auch in solchen Fällen, aus Messungen an Zellen ohne Diffusionspotential des Typs (28) bzw. (33) sichere Werte für die einzelnen Konstanten zu ermitteln[51].

Die Dissoziation von Aminosäuren wurde früher durch die Gleichungen

$$H_2N{\cdot}R{\cdot}COOH + H_2O \rightleftharpoons H_2N{\cdot}R{\cdot}COO^- + H_3O^+ ;\ K_{Säure} = \frac{[a_{R^-}][a_{H_3O^+}]}{[a_R]} \tag{61}$$

$$H_2N{\cdot}R{\cdot}COOH + H_2O \rightleftharpoons \overset{+}{H_2N}{\cdot}R{\cdot}COOH + OH^- ;\ K_{Base} = \frac{[a_{R^+}][a_{OH^-}]}{[a_R]} \tag{62}$$

beschrieben. Nach der Erkenntnis[52], daß die Aminosäuren infolge eines tautomeren Gleichgewichts im wesentlichen als *Zwitterionen*, d.h. als innere Salze, zu formulieren sind, faßt man die Aminosäuren in neuerer Zeit als zweibasische Säuren (Kationsäuren) auf, und formuliert die Dissoziation in folgender Weise:

$$\overset{+}{H_3N}{\cdot}R{\cdot}COOH + H_2O \rightleftharpoons \overset{+}{H_2N}{\cdot}R{\cdot}COO^- + H_3O^+ ;\ K_1 = \frac{[a_{R^\pm}][a_{H_3O^+}]}{[a_{R^+}]} \tag{63}$$

$$\overset{+}{H_3N}{\cdot}R{\cdot}COO^- + H_2O \rightleftharpoons H_2N{\cdot}R{\cdot}COO^- + H_3O^+ ;\ K_2 = \frac{[a_{R^-}][a_{H_3O^+}]}{[a_{R^\pm}]} \tag{64}$$

Ein Vergleich der so definierten Konstanten zeigt, daß

$$K_2 \equiv K_{Säure} \quad \text{und} \quad K_1 \equiv \frac{P}{K_{Base}} \tag{65}$$

wenn man mit

$$P \equiv [a_{H_3O^+}][a_{OH^-}] \tag{66}$$

das Ionenprodukt des Wassers bezeichnet. In den Tabellen sind stets die mittels P auf K_1 und K_2 umgerechneten Werte angegeben[53].

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II. THE USE OF THE TABLES

Column 2 gives the name, chemical formula and thermodynamic dissociation constant K of the acid or the so-called pK value ($pK \equiv -\log K$). Only when the thermodynamic constant is not stated are constants introduced which have not been extrapolated to ionic strength $I=0$. For very exact measurements the concentration scale in mole/1000 g of water or in mole/l. is indicated by (m) or (c) respectively.

Column 3 gives the temperature of the measurements in °C.

Column 4 states the range of concentration over which measurements were made:

$\mathcal{J} \equiv \frac{1}{2}\sum c_i z_i^2 \equiv$ ionic strength (I)
$c \equiv$ concentration in mole/l.
$m \equiv$ concentration in mole/1000 g of water
$\varkappa \equiv$ the specific conductance of the water used, in 10^{-6} ohm^{-1} cm^{-1}.

Column 5 indicates the methods of measurement employed, the calculation procedure used to evaluate the measurements, and any corrections which were taken into consideration. This information is arranged systematically and abbreviations are used. It proved impossible to provide complete descriptions of all the variations of these procedures and the cited literature must therefore be consulted for details.

Conductometric methods

L1 Measurements in solutions of salt and acid
L2 Measurements in solutions of acid only

Electrometric methods

Measurements in cells without diffusion potentials

E1a Method of Harned and Ehlers (see Part I)
E1b Method of Harned and Owen (see Part I)
E1c Determination of c_{H^+} by means of cells without diffusion potentials; for calculation of K, see, e.g. Jones and Soper, *J. Chem. Soc.*, **1936**, 133
E1d Method of Bates, *J. Am. Chem. Soc.*, **70**, 1579 (1948). (Method for the determination of K_1 and K_2 for dibasic acids)

Measurements in approximately symmetrical cells with diffusion potentials

E2a Method of Owen (see Part I)
E2b Method of Larsson and Adell (see Part I)
E2c Similar to **E2b** but a second weak acid of known dissociation constant is used instead of a strong acid. The technique yields the ratio of the two constants (see, e.g. Everett and Landsman, *Proc. Roy. Soc.*, **A215**, 403 (1952))

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II. ERKLÄRUNGEN ZUR BENUTZUNG DER TABELLEN

Spalte 2 enthält den Namen, die chemische Formel und die thermodynamische Dissoziationskonstante K der Säure bzw. den sog. pK-Wert (p$K \equiv -\log K$). Nur wenn die thermodynamische Konstante nicht angegeben war, werden auch Konstanten angeführt, die nicht auf Ionenstärke Null extrapoliert waren. Bei sehr genauen Messungen ist die benutzte Konzentrationsskala durch (m) bzw. (c) in Mol/1000 g Wasser bzw. Mol/Liter angegeben.

Spalte 3 enthält die Meßtemperatur in °C.

Spalte 4 enthält Angaben über den Konzentrationsbereich, in dem die Messungen stattfanden:

$J \equiv \frac{1}{2} \sum c_i z_i^2 \equiv$ Ionenstärke
$c \equiv$ Konzentration in Mol/Liter
$m \equiv$ Konzentration in Mol/1000 g Wasser
$\varkappa \equiv$ ist die spezifische Leitfähigkeit des benutzten Wassers in 10^{-6} Ohm^{-1} cm^{-1}.

Spalte 5 enthält Angaben über die benutzte Meßmethode, das zur Auswertung der Messungen verwendete Rechenverfahren und über evtl. berücksichtigte Korrekturen. Diese Angaben sind im folgenden systematisch geordnet und mit Abkürzungen versehen, die jeweils in der Tabelle angegeben sind. Auf die ausführliche Beschreibung aller Variationen dieser Verfahren wird verzichtet; dafür muß auf die zitierte Literatur verwiesen werden.

Konduktometrische Methoden

L1 Messungen an Salz- und Säurelösungen
L2 Messungen nur an Säurelösungen

Elektrometrische Methoden

Messungen an Zellen ohne Diffusionspotential

E1a Methode nach Harned u. Ehlers (vgl. Teil I)
E1b Methode nach Harned u. Owen (vgl. Teil I)
E1c Bestimmung von $c_{H_3O^+}$ mit Hilfe von Zellen ohne Diffusionspotential; Berechnung von K_c (vgl. z.B. Jones u. Soper, *J. Chem. Soc.* **1936**, 133)
E1d Methode nach Bates: *J. Am. Chem. Soc.* **70**, 1579 (1948). (Methode zur Bestimmung von K_1, K_2 für zweibasische Säuren)

Messungen an angenähert symmetrischen Zellen mit Diffusionspotential

E2a Methode nach Owen (vgl. Teil I)
E2b Methode nach Larsson u. Adell (vgl. Teil I)
E2c Ähnlich wie **E2b**, aber anstatt einer starken Säure wird eine zweite schwache Säure verwendet, deren Dissoziationskonstante bekannt ist. Das Verfahren führt zum Verhältnis der beiden Konstanten (vgl. z.B. Everett u. Landsman, *Proc. Roy. Soc.* **A215**, 403 (1952))

Measurements in unsymmetrical cells with diffusion potentials

E3a pH measurements in buffer solutions of weak electrolytes (see Part I)
E3b Measurements of the change in pH during titrations (see Speakman, *J. Chem. Soc.*, **1940**, 855)
E3c Differential potentiometric methods (see Part I)

Catalytic methods

Kat On account of the uncertainties inherent in constants estimated by catalytic measurements (see Part I), no details of the numerous catalytic methods are given

Optical methods (see Part I)

O1 Direct determination of the degree of dissociation by extinction measurements in solutions of weak acids and salts
O2 Colorimetric determination with an indicator, the dissociation constant of which is known
O3 Colorimetric determination with an indicator which has been calibrated with a buffer solution of known pH
O4 Method of v. Halban and Brüll
O5 Light absorption measurements combined with electrometric measurements

Methods of calculation

Evaluation of conductance measurements (see Part I)

R1a Method of Davies
R1b Method of MacInnes
R1c Method of Fuoss and Kraus
R1d Method of Shedlovsky

Evaluation of differential potentiometric measurements

R2a Method of Kilpi (*Z. physik. Chem.*, **173**, 223, 427 (1935), **175**, 239, (1936))
R2b Method of Hahn and Klockmann (*Z. physik. Chem.* **146**, 373, (1930))
R2c Method of Grunwald (*J. Am. Chem. Soc.*, **73**, 4934, (1951); *cf.* Kilpi, *J. Am. Chem. Soc.*, **74**, 5296, (1952))

Calculation of constants of polybasic acids

In view of the number of these methods of calculation, only those which are frequently applied are mentioned. In those cases where the calculations have been suitably modified for a particular problem, the original paper concerned should be consulted.

R3a Method of Kolthoff and Bosch (*Rec. trav. chim.* **47**, 861 (1928); *cf.* Speakman, *J. Chem. Soc.* **1940**, 855)
R3b Method of Auerbach and Smolczyk (*Z. physik. Chem.* **A110**, 83 (1924); *cf.* Britton, *J. Chem. Soc.* **127**, 1896 (1925))
R3c Method of Britton (*J. Chem. Soc.* **127**, 1896, (1925))
R3d Method of Speakman (*J. Chem. Soc.* **1940**, 855)

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Messungen an unsymmetrischen Zellen mit Diffusionspotential

E3a pH-Messungen an Pufferlösungen des schwachen Elektrolyten (vgl. Teil I)

E3b Messung des pH-Verlaufes bei Titration (vgl. Speakman, *J. Chem. Soc.* **1940**, 855)

E3c Differential-potentiometrische Methoden (vgl. Teil I)

Katalytische Methoden

Kat. In Anbetracht der prinzipellen Unsicherheiten, die den aus katalytischen Messungen ermittelten Konstanten anhaften (vgl. Teil I), wird keine Detaillierung der mannigfaltigen katalytischen Methoden vorgenommen

Optische Methoden (vgl. Teil I)

O1 Direkte Bestimmung des Dissoziationsgrades durch Extinktionsmessungen an Lösungen der schwachen Säure und des Salzes

O2 Kolorimetrische Bestimmung mit einem Indikator, dessen Dissoziationskonstante bekannt ist

O3 Kolorimetrische Bestimmung mit einem Indikator, der mit Pufferlösungen von bekannten pH geeicht wird

O4 Methode nach v. Halban und Brüll

O5 Lichtabsorptionsmessungen kombiniert mit elektrometrischen Messungen

Rechenverfahren

Zur Auswertung von Leitfähigkeitsmessungen (vgl. Teil I)

R1a Methode nach Davies

R1b Methode nach MacInnes

R1c Methode nach Fuoss u. Kraus

R1d Methode nach Shedlovsky

Zur Auswertung differential-potentiometrischer Messungen

R2a Methode nach Kilpi (*Z. physik. Chem.* **173**, 223, 427 (1935); **175**, 239 (1936))

R2b Methode nach Hahn u. Klockmann (*Z. physik. Chem.* **146**, 373 (1930))

R2c Methode nach Grunwald (*J. Am. Chem. Soc.* **73**, 4934 (1951); Kritik bei Kilpi *J. Am. Chem. Soc.* **74**, 5296 (1952))

Zur Berechnung der Konstanten mehrbasischer Säuren

Wegen der Vielfalt der benutzten Rechenmethoden werden hier nur die häufiger verwendeten angeführt. In den Fällen, wo die Rechnung auf das spezielle Problem zurechtgeschnitten ist, muß auf die betreffende Originalarbeit verwiesen werden.

R3a Methode nach Kolthoff u. Bosch (*Rec. trav. chim.* **47**, 861 (1928); Kritik bei Speakman, *J. Chem. Soc.* **1940**, 855)

R3b Methode nach Auerbach u. Smolczyk (*Z. physik. Chem.* **A110**, 83 (1924); Kritik bei Britton, *J. Chem. Soc.* **127**, 1896 (1925))

R3c Methode nach Britton (*J. Chem. Soc.* **127**, 1896 (1925))

R3d Methode nach Speakman (*J. Chem. Soc.* **1940**, 855)

R3e Method of Chandler for the calculation of the primary constants from conductivity measurements (*J. Am. Chem. Soc.* **30**, 694, (1908))

Treatment of diffusion potentials

D1 With salt bridges, the residual diffusion potential being ignored
D2 Method of Bjerrum (see Part I)
D3 Calculation of diffusion potential (see Part I)

Corrections

Consideration of the hydrolysis of salts in conductivity measurements

K1a Method of MacInnes and Shedlovsky; addition of a slight excess of free acid (*J. Am. Chem. Soc.* **54**, 1429 (1932))
K1b Method of Jeffery and Vogel; calculated corrections with the help of K_{H_2O} and an approximate value for K_a (*J. Chem. Soc.* **1932**, 2829; *cf.* Ives, *J. Chem. Soc.* **1933**, 313)
K1c Method of Jeffery and Vogel; correction for hydrolysis together with that for the solvent (*Phil. Mag.* **18**, 901 (1934))
K1d Method of Ives; correction for hydrolysis together with that for the solvent (*J. Chem. Soc.*, **1933**, 313)
K1e Method of Davies; correction for hydrolysis together with that for the solvent (*Trans. Faraday Soc.*, **28**, 607 (1932); *cf.* Banks and Davies, *J. Chem. Soc.* **1938**, 73)
K1f Average of results obtained by method **K1e** from which $\varkappa_{H_2O}$ is completely eliminated (Banks and Davies, *J. Chem. Soc.* **1938**, 73)

Correction for solvent

K2a "Normal correction", where $\varkappa_{H_2O}$ is not eliminated for acids and is completely eliminated for salts
K2b $\varkappa_{H_2O}$ is completely eliminated for acid and salt solutions
K2c Method of MacInnes and Shedlovsky (*J. Am. Chem. Soc.* **54**, 1429 (1932))
K2d Method of Jeffery and Vogel (*J. Chem. Soc.* **1933**, 1637)
K2e Method of Dippy and Williams (*J. Chem. Soc.* **1934**, 161, 1888)

Column 6 contains the assessment, which is described in the introduction, of the reliability of the constant quoted. Where possible, the basis of this assessment is briefly stated.

Column 7 contains the appropriate reference to the literature given in Part V.

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R3e Methode nach Chandler (zur Berechnung der primären Konstanten aus Leitfähigkeitsmessungen) (*J. Am. Chem. Soc.* **30**, 694 (1908))

Behandlung der Diffusionspotentiale

D1 Mit Salzbrücke, restliche Diffusionspotentiale vernachlässigt
D2 Methode nach Bjerrum (vgl. Teil I)
D3 Berechnung der Diffusionspotentiale (vgl. Teil I)

Korrekturen

Berücksichtigung der Hydrolyse von Salzen bei Leitfähigkeitsmessungen

K1a Verfahren nach MacInnes u. Shedlovsky (Zusatz eines geringen Überschußes freier Säure) (*J. Am. Chem. Soc.* **54**, 1429 (1932))
K1b Verfahren nach Jeffery u. Vogel (rechnerische Korr. mit Hilfe von K_{H_2O} und einem ungefähren Wert für K_c) (*J. Chem. Soc.* **1932**, 2829; Kritik bei Ives, *J. Chem. Soc.* **1933**, 313)
K1c Verfahren nach Jeffery u. Vogel (Korr. zusammen mit Solvenskorr.) (*Phil. Mag.* **18**, 901 (1934))
K1d Verfahren nach Ives (Korr. zusammen mit Solvenskorr.) (*J. Chem. Soc.* **1933**, 313))
K1e Verfahren nach Davies (Korr. zusammen mit Solvenskorr.) (*Trans. Faraday Soc.* **28**, 607 (1932); Kritik bei Banks u. Davies, *J. Chem. Soc.* **1938**, 73)
K1f Mittelwerte aus den nach Methode **K1e** erhaltenen und solchen, bei denen $\varkappa_{H_2O}$ voll abgezogen wird (Banks u. Davies, *J. Chem. Soc.* **1938**, 73)

Solvenskorrektur

K2a "Normale Korrektur", bei der $\varkappa_{H_2O}$ bei Säuren nicht und bei Salzen voll abgezogen wird
K2b $\varkappa_{H_2O}$ wird bei Säure- und Salzlösungen voll abgezogen
K2c Verfahren nach MacInnes u. Shedlovsky (*J. Am. Chem. Soc.* **54**, 1429 (1932))
K2d Verfahren nach Jeffery u. Vogel (*J. Chem. Soc.* **1933**, 1637)
K2e Verfahren nach Dippy u. Williams (*J. Chem. Soc.* **1934**, 161, 1888)

Spalte 6 enthält die in der Einführung beschriebene Schätzung der Zuverlässigkeit der angeführten Konstanten. In Fällen, wo dies möglich war, wird eine stichwortartige Begründung für diese Schätzung angegeben.

Spalte 7 enthält die zugehörige Literaturangabe aus Abschnitt V.

III. ARRANGEMENT OF ACIDS IN THE TABLES

Notation

1. Aliphatic and alicyclic carboxylic acids

111. Unsubstituted fatty acids
112. Unsubstituted unsaturated fatty acids
113. Unsubstituted alicyclic fatty acids
121. Substituted with halogen or cyanogen groups
122. Substituted with alcohol or ether groups
123. Substituted with amino or alkylamino groups
124. Substituted with keto or aldehyde groups
125. Substituted with other, or several, substituents (see also **22**)

2. Aromatic carboxylic acids

21. *Carboxyl group on the aromatic nucleus*

211. Simple or alkyl-substituted
212. Halogen- and cyanogen-substituted
213. Hydroxyl-substituted
214. Nitro-substituted
215. Amino-substituted
216. Ether-substituted
217. Others

22. *Carboxyl group on the side-chain*

221. Unsubstituted
222. Halogen- and cyanogen-substituted
223. Hydroxyl-substituted
224. Nitro-substituted
225. Amino-substituted
226. Ether-substituted
227. Others

3. Phenolic acids

31. Simple and alkyl-substituted
32. Halogen- and cyanogen-substituted
33. Nitro-substituted
34. Amino-substituted
35. Ether-substituted
36. Others

4. Other acids

41. Sulfonic acids
42. Phosphoric acid esters, phosphonic acids, phosphinic acids

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III. ANORDNUNG DER SÄUREN IN DEN TABELLEN

Bezeichnung

1. Aliphatische und alizyklische Carbonsäuren

111. Unsubstituierte Fettsäuren
112. Unsubstituierte ungesättigte Fettsäuren
113. Unsubstituierte alizyklische Säuren
121. Substituiert mit Halogen- oder Cyangruppen
122. Substituiert mit Alkohol- oder Äthergruppen
123. Substituiert mit Amino- bzw. Alkylaminogruppen
124. Substituiert mit Keto- oder Aldehydgruppen
125. Substituiert mit sonstigen oder mehreren Substituenten (s.a. **22**)

2. Aromatische Carbonsäuren

21. *mit Carboxylgruppe am aromatischen Kern*
211. Einfache oder Alkylsubstituierte
212. Halogen- und Cyansubstituierte
213. Hydroxylsubstituierte
214. Nitrosubstituierte
215. Aminosubstituierte
216. Äthersubstituierte
217. Sonstige

22. *mit Carboxylgruppe an der Seitenkette*
221. Unsubstituierte
222. Halogen- und Cyansubstituierte
223. Hydroxylsubstituierte
224. Nitrosubstituierte
225. Aminosubstituierte
226. Äthersubstituierte
227. Sonstige

3. Phenolische Säuren

31. Einfache und Alkylsubstituierte
32. Halogen- und Cyansubstituierte
33. Nitrosubstituierte
34. Aminosubstituierte
35. Äthersubstituierte
36. Sonstige

4. Sonstige Säuren

41. Sulfonsäuren
42. Phosphorsäureester, Phosphonsäuren, Phosphinsäuren

Notation

43. Arsinic acids
44. Boro-, seleno- and other acids

5. Special types

51. Indicators and dyestuffs
52. Unclassified organic acids

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Bezeichnung

43. Arsinsäuren
44. Bor-, Selen- und sonstige Säuren

5. Sondergruppen

51. Indikatoren und Farbstoffsäuren
52. Unklassifizierte organische Säuren

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IV. TABLES—TABELLEN

Bezeichnung I11–I11 **111** No. 1–2

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
1	Ameisensäure: HCOOH					
	(c) $1{,}79 \cdot 10^{-4}$	18	$\varkappa = 2$ $\bar{f} = 0{,}005$ bis $0{,}02$	**E2b**	zuv.	L13
	(m) $1{,}633 \cdot 10^{-4}$	0	$\bar{f} = 0{,}01$ bis $0{,}2$	**E1a**	s. zuv.	H16
	1,691	5				
	1,728	10				
	1,749	15				
	1,765	20				
	1,772	25				
	1,768	30				
	1,747	35				
	1,716	40				
	1,685	45				
	1,650	50				
	1,607	55				
	1,551	60				
	(m) $1{,}77 \cdot 10^{-4}$	25	$\bar{f} = 0{,}005$ bis 3	**E1b**	s. zuv.	H19
	(c) $1{,}86 \cdot 10^{-4}$	18	$\varkappa = 0{,}7$ $\bar{f} = 0{,}001$ bis $0{,}1$	**L1** **R1b**	rel. zuv. A in $\log f = -A\sqrt{\bar{f}}$ hat nicht den theoretischen Wert. Messungen bei kleinsten Konzentrationen unsicher.	D1
	(c) $1{,}825 \cdot 10^{-4}$	25	$c = 0{,}0002$ bis $0{,}01$	**L1** **R1b**	rel. zuv. Keine genauen Angaben über Solvens- u. Hydrolyskorr.	S5
	(c) $1{,}82 \cdot 10^{-4}$	25	$\bar{f} = 0{,}004$ bis $0{,}0025$	**E3c** **R2c** **D1**	rel. zuv. bis unsicher. Mangelhafte Rechenmethode. Neigung der Titrationskurve unsicher. Diffusionspotentiale.	G23
					Weitere Messungen: B18, B32	

2 Essigsäure: CH_3COOH

(*m*)	1,635·10^{-5}	0	$\varkappa = 1$	**E1a**	s. zuv.	H13
	1,699	5	$\mathcal{I} = 0{,}01$ bis 2		Für E_0 unsicherere Werte bei 0° und 35° verwendet als bei H14 (s. u.)	
	1,727	10				
	1,743	15				
	1,751	20				
	1,754	25				
	1,755	30				
	1,750	35				
(*m*)	1,657·10^{-5}	0	$\varkappa = 1$	**E1a**	s. zuv.	H14
	1,700	5	$\mathcal{I} = 0{,}01$ bis 0,2			
	1,729	10				
	1,745	15				
	1,753	20				
	1,754	25				
	1,750	30				
	1,728	35				
	1,703	40				
	1,670	45				
	1,633	50				
	1,589	55				
	1,542	60				
(*c*)	1,734·10^{-5}	18	$\varkappa = 2$	**E2b**	zuv.	L12
			$\mathcal{I} = 0{,}01$			
(*c*)	1,754·10^{-5}	20	$\varkappa = 1{,}0$	**E3c**	rel. zuv.	K14
			$\mathcal{I} = 0{,}0004$ bis 0,005	**R2a**		
				D1		
(*m*)	1,75·10^{-5}	25	$\mathcal{I} = 0{,}02$ bis 3	**E1b**	s. zuv.	H19
(*c*)	1,73·10^{-5}	25	$\mathcal{I} = 0{,}0015$ bis 0,0055	**E3c**	rel. zuv. bis unsicher.	G23
	1,77	25		**R2c**	Die zwei verschiedenen Werte mit Kalomel bzw. Ag/AgCl-Elektrode erhalten. Mangelhafte Rechenmethode. Neigung der Titrationskurve rel. unsicher. Diffusionspotentiale.	
				D1		

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	(*r*) 1,759·10⁻⁵	25	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}0008$ bis $0{,}004$	**L1** u. **L2** abnl. **R1a** abnl. **R1c** **K1d**	rel. zuv. bis zuv. Apparative Mängel (Erdung, Parkereffekt möglich, Wasserthermostat).	I2
	(*s*) 1,753·10⁻⁵	25	$\varkappa = 0{,}2$ $\mathcal{J} = 0{,}0001$ bis $0{,}004$	**L1** **R1b** **K1a** **K2c**	s. zuv.	M5
	(*s*) 1,76·10⁻⁵	25	$\varkappa = 1$ $\mathcal{J} = 0{,}001$ bis $0{,}03$	**L1** **R1a** **K2e**	rel. zuv. Apparative Mängel (Glaszellen, Parkereffekt möglich, Wasserthermostat). Unsichere Solvenskorr. Keine Angaben über Hydrolysekorr.	D18
	(*m*) 1,8·10⁻⁵	25	$\mathcal{J} \geq 0{,}001$	**O2**	rel. zuv. Experimentelle Unsicherheiten. Konstante von Bromphenolblau verwendet (vgl. K3). Wenig Angaben.	K5
	(*c*) 1,764·10⁻⁵	25	$\varkappa = 0{,}4$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **K2d** **K1b** **R1b**	rel. zuv. Apparative Mängel (Zelle). Unsichere Korr. Verwendung empirischer "n-Formel".	J3
	(*c*) 1,785·10⁻⁵	25	$\varkappa = 1$ $\mathcal{J} = 0{,}002$ bis $0{,}07$	**L1** **R1b**	rel. zuv. A in $\log f_\pm = -A\sqrt{\mathcal{J}}$ hat nicht den theoretischen Wert; daneben Viskositätskorr. eingeführt. Meßdaten bei kleinsten Konz. unsicher.	D1
	(*c*) 1,765·10⁻⁵	25	$\varkappa = 1$ $\mathcal{J} = 0{,}002$ bis $0{,}07$	**L1** **R1b**	rel. zuv. A-Werte zeigen Gang mit Konz., angegebener Wert ist ein Mittelwert.	M3
	(*c*) 1,759·10⁻⁵	25	$\varkappa = 1$ $\mathcal{J} = 0{,}0002$ bis $0{,}002$	**L1** **K2a** **R1b**	zuv. bis rel. zuv. Apparative Mängel (Glaszellen). Unsichere Solvenskorr.	S6

	(*c*) 1,706·10⁻⁵	25	$\mathcal{J}$ = 0,003 bis 0,03	**O2**	rel. zuv. Relative Konstanten gegen Bromkresolgrün bestimmt. *K* für letzteres nicht direkt gemessen, sondern schrittweise aus dem Konstantenverhältnis mehrerer anderer Säuren ermittelt. Keine Korr. für Reaktion d. Puffermischung mit H_2O und der zugesetzten Indikatorsäure.	M21
	(*m*) 1,752·10⁻⁵	25	$\mathcal{J}$ = 0,02 bis 0,05	ähnl. **E1a**	s. zuv. Statt Puffergemisch aus Essigsäure und Acetat Mischung aus Acetat u. Ameisensäure. Mit bekanntem *K* für letztere (H16) wird *K* für Essigsäure berechnet.	B13
					Weitere Messungen: A6; A14; B18; B32; B51; C20; D3; D4; E5; H1; H2; H3; H21; I3; J2; K13; K15; K27; L1; M27; P4; O4; S22.	
3	Propionsäure: $CH_3{\cdot}CH_2{\cdot}COOH$					
	(*m*) 1,274·10⁻⁵ 1,305 1,326 1,336 1,338 1,336 1,326 1,310 1,284 1,257 1,229 1,195 1,160	0 5 10 15 20 25 30 35 40 45 50 55 60	$\mathcal{J}$ = 0,01 bis 0,09	**E1a**	s. zuv.	H15
	(*c*) 1,32·10⁻⁵	18	$\varkappa$ = 2 $\mathcal{J}$ = 0,01 bis 3	**E2b**	zuv.	L13
	(*c*) 1,343·10⁻⁵	25	$\varkappa$ = 0,2 $\mathcal{J}$ = 0,00003 bis 0,2	**L1** **R1a** **R1d**	zuv. Keine Solvenskorr. Werte bei kleinsten Konz. unsicher. Apparative Mängel (Glaszellen).	B21

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
	(c) $1{,}285 \cdot 10^{-5}$	0	$\varkappa = 1$	**E2c**	Aus Verhältnis der Diss. Konstante zu der von Essigsäure. Für letztere Werte von Harned u. Ehlers (H14) verwendet.	
	$1{,}329$	10	$\bar{\gamma} = 0{,}05$ bis $0{,}2$			
	$1{,}337$	20				
	$1{,}325$	30				
	$1{,}281$	40				
	$1{,}221$	50				
	$1{,}148$	60				
	(m) $1{,}32 \cdot 10^{-5}$	20	$\varkappa = 0{,}6$	**O4**	rel. zuv.	K34
	$1{,}28$		$\bar{\gamma} = 0{,}0003$ bis $0{,}0004$		1. Wert mit 2,4-Dinitrophenol als Indikator, 2. Wert m. Bromphenolblau. Temp. Schwankungen u. allgem. Meßfehler.	
					Weitere Messungen: B33; D3.	
4	n-Buttersäure: $CH_3(CH_2)_2COOH$					
	(m) $1{,}563 \cdot 10^{-5}$	0	$\bar{\gamma} = 0{,}015$ bis $0{,}1$	**E1a**	s. zuv.	H22
	$1{,}574$	5				
	$1{,}576$	10				
	$1{,}569$	15				
	$1{,}542$	20				
	$1{,}515$	25				
	$1{,}484$	30				
	$1{,}439$	35				
	$1{,}395$	40				
	$1{,}347$	45				
	$1{,}302$	50				
	$1{,}252$	55				
	$1{,}199$	60				
	(c) $1{,}53 \cdot 10^{-5}$	18	$\varkappa = 2$	**E2b**	zuv.	L13
			$\bar{\gamma} = 0{,}01$ bis $0{,}03$			
	(c) $1{,}50 \cdot 10^{-5}$	25	$\varkappa = 1$	**L1**	rel. zuv.	D9
			$\bar{\gamma} = 0{,}003$ bis $0{,}012$	**R1a** **K2e**	Wie bei iso-Buttersäure (D9)	

	(*c*) 1,518·10⁻⁵	25	$\mathcal{I}$ = 0,001 bis 0,02	**L1** **R1b** **(K1a)**	rel. zuv. Keine genauen Angaben über Solvens- u. Hydrolysekorr.	S5
	(*c*) 1,503·10⁻⁵	25	$\varkappa$ = 0,03 bis 0,5 $\mathcal{I}$ = 0,00003 bis 0,2	**L1** **R1a** **R1d**	s. zuv.	B21
5	iso-Buttersäure: $(CH_3)_2CH{\cdot}COOH$					
	(*c*) 1,497·10⁻⁵	0	$\varkappa$ = 1	**E2c**	s. zuv.	E10
	1,489	10	$\mathcal{I}$ = 0,02 bis 0,2		Wie bei Propionsäure (E10)	
	1,447	20				
	1,301	30				
	1,208	40				
	1,110	50				
	1,017	60				
	(*c*) 1,44·10⁻⁵	18	$\varkappa$ = 2 $\mathcal{I}$ = 0,01 bis 3	**E2b**	zuv.	L13
	(*c*) 1,38·10⁻⁵	25	$\varkappa$ = 1 $\mathcal{I}$ = 0,01 bis 0,02	**L1** **R1a** **K2e**	rel. zuv. Apparative Mängel (Glaszellen, Parkereffekt möglich, Wasserthermostat). Unsichere Solvenskorr. Keine Angaben über Hydrolysekorr.	D9
6	n-Valeriansäure: $CH_3{\cdot}(CH_2)_3{\cdot}COOH$					
	(*c*) 1,504·10⁻⁵	0	$\varkappa$ = 1	**E2c**	s. zuv.	E10
	1,501	10	$\mathcal{I}$ = 0,05 bis 0,2		Wie bei Propionsäure (E10).	
	1,463	20				
	1,409	30				
	1,329	40				
	1,241	50				
	1,147	60				
	(*c*) 1,51·10⁻⁵	18	$\varkappa$ = 2 $\mathcal{I}$ = 0,01 bis 0,03	**E2b**	rel. zuv. bis unsicher, da verwendete Säure nicht rein war.	L13
	(*c*) 1,38·10⁻⁵	25	$\varkappa$ = 1 $\mathcal{I}$ = 0,003 bis 0,01	**L1** **R1a** **K2e**	rel. zuv. Wie bei iso-Buttersäure (D9)	D9

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
7	iso-Valeriansäure: $(CH_3)_2CH{\cdot}CH_2{\cdot}COOH$					
	(c) $1{,}879{\cdot}10^{-5}$	0	$\varkappa = 1$	**E2c**	s. zuv.	E10
	$1{,}810$	10	$J = 0{,}05$ bis $0{,}2$		Wie bei Propionsäure (E10)	
	$1{,}709$	20				
	$1{,}605$	30				
	$1{,}477$	40				
	$1{,}345$	50				
	$1{,}216$	60				
	(c) $1{,}70{\cdot}10^{-5}$	18	$\varkappa = 0{,}3$	**E2b**	zuv.	L7
			$J = 0{,}01$ bis 3			
	(c) $1{,}67{\cdot}10^{-5}$	25	$\varkappa = 1$	**L1**	rel. zuv.	D9
			$J = 0{,}002$ bis $0{,}01$	**R1a**	Wie bei iso-Buttersäure (D9)	
				K2e		
8	Trimethyl-Essigsäure: $(CH_3)_3C{\cdot}COOH$					
	(c) $9{,}4{\cdot}10^{-6}$	18	$\varkappa = 2$	**E2b**	zuv.	L13
			$J = 0{,}01$ bis 3			
	(c) $9{,}65{\cdot}10^{-6}$	0	$\varkappa = 1$	**E2c**	s. zuv.	E10
	$9{,}68$	10	$J = 0{,}05$ bis $0{,}2$		Wie bei Propionsäure (E10)	
	$9{,}44$	20				
	$9{,}11$	30				
	$8{,}58$	40				
	$7{,}97$	50				
	$7{,}32$	60				
	(c) $8{,}91{\cdot}10^{-6}$	25	$\varkappa = 1$	**L1**	rel. zuv.	D9
			$J = 0{,}002$ bis $0{,}007$	**R1a**		
				K2e		
9	Methyl-Äthyl-Essigsäure: $CH_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOH$					
	(c) $1{,}56{\cdot}10^{-5}$	18	$\varkappa = 0{,}3$	**E2b**	zuv.	L7
			$J = 0{,}01$ bis 3			

10	n-Capronsäure: $CH_3 \cdot (CH_2)_4 \cdot COOH$					
	(*c*) $1{,}43 \cdot 10^{-5}$	18	$\varkappa = 2$ $\mathcal{J} = 0{,}01$ bis 3	**E2b**	zuv.	L13
	(*c*) $1{,}32 \cdot 10^{-5}$	25	$\varkappa = 1$ $\mathcal{J} = 0{,}003$ bis 0,01	**L1** **R1a** **K2e**	rel. zuv. Wie bei iso-Buttersäure (D9)	D9
	(*c*) $1{,}445 \cdot 10^{-5}$ 1,448 1,416 1,364 1,287 1,201 1,110	0 10 20 30 40 50 60	$\varkappa = 1$ $\mathcal{J} = 0{,}05$ bis 0,2	**E2c**	rel. zuv. Aus Verhältnis der Dissoziationskonstanten zu der von Essigsäure. Für letztere Werte von Harned u. Ehlers (H14) verwendet. Gemessene E.M.K. war zeitabhängig. Nicht zu übersehen, wie groß hierdurch bedingter Fehler ist.	E10
	(*c*) $1{,}44 \cdot 10^{-5}$	18	$\mathcal{J} = 0{,}001$ bis 0,01	**E3a** **R3a** **D2**	rel. zuv. bis unsicher. pH-Wert der Vergleichslösung (0,01n HCl + 0,09n KCl) unsicher. Diffusionspotentiale.	K29
11	iso-Capronsäure: $(CH_3)_2CH \cdot (CH_2)_2 \cdot COOH$					
	(*c*) $1{,}456 \cdot 10^{-5}$	18	$\varkappa = 2$ $\mathcal{J} = 0{,}01$ bis 3	**E2b**	zuv.	L13
	(*c*) $1{,}491 \cdot 10^{-5}$ 1,491 1,455 1,402 1,322 1,235 1,141	0 10 20 30 40 50 60	$\varkappa \leqslant 1$ $\mathcal{J} = 0{,}05$ bis 0,2	**E2c**	rel. zuv. Wie bei n-Capronsäure (E10)	E10
12	Methyl-n-Propyl-Essigsäure: $CH_3 \cdot (CH_2)_2 \cdot CH(CH_3) \cdot COOH$					
	(*c*) $1{,}62 \cdot 10^{-5}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis 3	**E2b**	zuv.	L7
13	β-Methyl-β-Äthyl-Propionsäure: $CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot COOH$					
	(*c*) $1{,}46 \cdot 10^{-5}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis 3	**E2b**	zuv.	L7

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
14	Dimethyl-Äthyl-Essigsäure: $CH_3{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}COOH$					
	(c) $9{,}3{\cdot}10^{-6}$	18	$\varkappa = 0{,}3$ $\bar{\gamma} = 0{,}01$ bis 3	**E2b**	zuv.	L7
15	Diäthyl-Essigsäure: $(CH_3{\cdot}CH_2)_2CH{\cdot}COOH$					
	(c) $2{,}381{\cdot}10^{-5}$	0	$\varkappa = 1$ $\bar{\gamma} = 0{,}05$ bis 0,2	**E2c**	s. zuv. Wie bei Propionsäure (E10)	E10
	2,169	10				
	1,948	20				
	1,744	30				
	1,540	40				
	1,353	50				
	1,181	60				
	(c) $1{,}775{\cdot}10^{-5}$	25	$\varkappa = 1$ $\bar{\gamma} = 0{,}001$ bis 0,007	**L1** **R1a** **K2e**	rel. zuv. Wie bei iso-Buttersäure (D9)	D9
	(c) $1{,}93{\cdot}10^{-5}$	18	$\varkappa = 0{,}3$ $\bar{\gamma} = 0{,}01$ bis 3	**E2b**	zuv.	L7
16	Önanthsäure: $CH_3{\cdot}(CH_2)_5{\cdot}COOH$					
	(c) $1{,}28{\cdot}10^{-5}$	25	$\varkappa = 1$ $\bar{\gamma} = 0{,}002$ bis 0,005	**L1** **R1a** **K2e**	rel. zuv. Wie bei iso-Buttersäure (D9)	D9
	(c) $1{,}42{\cdot}10^{-5}$	18	$\varkappa = 2$ $\bar{\gamma} = 0{,}01$ bis 0,03	**E2b**	unsicher Die verwendete Säure hatte ein Äquivalentgewicht von 131,5 (theoret. 130,1).	L13
17	tert.-Amyl-Essigsäure: $(CH_3)_3C{\cdot}(CH_2)_2{\cdot}COOH$					
	(c) $1{,}63{\cdot}10^{-5}$	18	$\varkappa = 0{,}3$ $\bar{\gamma} = 0{,}01$ bis 0,03	**E2b**	zuv.	L7

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18	Äthyl-n-Propyl-Essigsäure: $CH_3{\cdot}(CH_2)_2{\cdot}CH(CH_2{\cdot}CH_3){\cdot}COOH$					
	(*c*) $1{,}96{\cdot}10^{-5}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis 3	**E2b**	zuv.	L7
19	Caprylsäure: $CH_3{\cdot}(CH_2)_6{\cdot}COOH$					
	(*c*) $1{,}275{\cdot}10^{-5}$	25	$\varkappa = 1$ $\mathcal{J} = 0{,}0005$ bis 0,015	**L1** **R1a** **K2e**	rel. zuv. Wie bei iso-Buttersäure (D9)	D9
20	Pelargonsäure: $CH_3{\cdot}(CH_2)_7{\cdot}COOH$					
	(*c*) $1{,}11{\cdot}10^{-5}$	25	$\varkappa = 1$ $\mathcal{J} = 0{,}0004$ bis 0,001	**L1** **R1a** **K2e**	rel. zuv. Wie bei iso-Buttersäure (D9)	D9
21	Oxalsäure: COOH·COOH					
	(*m*) K_2 $5{,}91{\cdot}10^{-5}$	0	$\varkappa = 1$ $\mathcal{J} = 0{,}025$ bis 0,16	**E1a**	rel. zuv. Ungenaue Korr. für weitere Dissoziation des Bioxalations (vgl. P7).	H17
	5,82	5				
	5,70	10				
	5,55	15				
	5,40	20				
	5,18	25				
	4,92	30				
	4,67	35				
	4,41	40				
	4,09	45				
	3,83	50				
	(*c*) K_1 $5{,}36{\cdot}10^{-2}$ K_2 $5{,}3{\cdot}10^{-5}$	25	$\mathcal{J} = 0{,}0002$ bis 0,03	**L1** **R1b**	K_1 rel. zuv. K_2 unsicher. Angewendetes Rechenverfahren führt per Definition zu konstantem K_1; daß auch für K_2 konstanter Wert erzielt wird, wird als Beweis für die Richtigkeit der Methode angesehen. Anwendung der D.H.-Gl. u. der Shedlovsky'schen für A_c bei den höheren Konzentrationen bedingt Unsicherheiten. Andrerseits stützt sich die Berechnung von K_1 gerade auf diese Konz.-Gebiete. K_2 wird als Korrekturgröße berechnet.	D1

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	(*m*) K_2 $6{,}30\cdot10^{-3}$	0	$\varkappa = 0{,}4$ bis $0{,}7$	**E1a**	zuv.	P7
	$6{,}21$	5	$\bar{J} = 0{,}05$ bis $0{,}7$			
	$6{,}05$	10				
	$5{,}87$	15				
	$5{,}67$	20				
	$5{,}41$	25				
	$5{,}16$	30				
	$4{,}88$	35				
	$4{,}59$	40				
	$4{,}28$	45				
	$3{,}99$	50				
	(*c*) K_1 $5{,}62\cdot10^{-2}$	20	$\bar{J} = 0{,}0002$ bis $0{,}001$	**E3b**	unsicher bis rel. zuv.	S27
	K_2 $5{,}89\cdot10^{-5}$			**D1**	Glaselektrode; Diffusionspotentiale.	
				R3d		
	(*m*) K_1 $5{,}0\cdot10^{-2}$	25	$\bar{J} = 0{,}007$ bis $0{,}26$	**E1a**	K_1 unsicher, K_2 rel. zuv.	P2
	K_2 $5{,}012\cdot10^{-5}$	25			Berechnung von K_1 (*m*) wegen Größe der Konstanten langwierig und ungenau. Bei Berechnung von K_2 wurde die Dissoziation des Bioxalations nicht berücksichtigt (vgl. H17 und P7). Wenig exp. Angaben.	
	$4{,}787$	30				
	$4{,}488$	35				
	(*c*) K_2 $7{,}1\cdot10^{-5}$	18	$\varkappa = 1{,}5$	**E2a**	unsicher.	L2
			$\bar{J} = 0{,}05$ bis $0{,}2$	**D2**	Extrapolation der K_c' durch Auftragen von log K_c' gegen $\sqrt[3]{\bar{J}}$. Diffusionspotentiale.	
	(*c*) K_1 $5{,}90\cdot10^{-2}$	25	$\bar{J} = 0{,}001$	**E3b**	unsicher.	G5
	(*c*) K_2 $6{,}40\cdot10^{-5}$			**D1**	Ungenaue Rechenmethoden (vgl. dazu aber I5). Extrapolation von log K_c auf $\bar{J}=0$ durch Auftragen gegen $\bar{J}$ (Verlauf folgt nicht der D.H.-Gl.) Diffusionspotentiale.	
				R3b		
	(*m*) K_1 $4{,}6\cdot10^{-2}$	25	$\bar{J} = 0{,}006$ bis $0{,}13$	**E1a**	unsicher.	P3
	$5{,}5$	30			Berechnung von K durch langwierige Approximationen. Dabei statt $f_{H_2O}\cdot f_{HO_4^-}$ der Ausdruck $f_H\cdot f_{Cl^-}$ verwendet.	
	$5{,}35$	35				

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						Weitere Messungen: B52; C21; D5; D6; H2; L3; S13; S22; S27.	
22	**Malonsäure: $COOH{\cdot}CH_2{\cdot}COOH$**						
	(*m*) K_2 2,140·10^{-6}	0	$\varkappa = 1$	**E1a**	s. zuv. bis zuv.		HB
	2,165	5	$\mathcal{J} = 0{,}005$ bis $0{,}23$				
	2,152	10					
	2,124	15					
	2,076	20					
	2,014	25					
	1,948	30					
	1,863	35					
	1,768	40					
	1,670	45					
	1,575	50					
	1,469	55					
	1,362	60					
	(*c*) K_1 1,397·10^{-3}	25	$\varkappa = 0{,}6$	**L1**	rel. zuv.		J6a
			$\mathcal{J} = 0{,}0001$ bis $0{,}01$	**R1b**	Störung durch zweite Dissoziationsstufe; apparative Mängel (Parkereffekt möglich); Unsicherheiten in der Bestimmung von Λ_{0HM^-} (nach empirischer Beziehung aus $\Lambda_{0M^{2-}}$ berechnet). Extrapolationskurve für log K_c durchläuft bei $\mathcal{J} \simeq 0{,}003$ ein Minimum, doch Werte bei $\mathcal{J} < 0{,}003$ vernachlässigt. Die Unsicherheiten in der Bestimmung von Λ_{0HM^-} sind nicht abzuschätzen.	
	(*c*) K_1 1,43·10^{-3}	25	$\mathcal{J} = 0{,}0015$ bis $0{,}006$	**E3b**	unsicher bis rel. zuv.		G7
	K_2 2,2·10^{-6}			**R3c**			
				D1			
	(*c*) K_1 1,49·10^{-3}	25	$\mathcal{J} = 0{,}001$ bis $0{,}05$	**E3b**	unsicher.		G5
	K_2 2,03·10^{-6}			**D1**	Wie bei Oxalsäure (G5)		
				R3b			
	(*c*) K_2 2,0·10^{-6}	18	$\varkappa = 1{,}5$ bis 2	**E3a**	unsicher.		L3
			$\mathcal{J} = 0{,}05$ bis $0{,}2$	**D2**	Wie bei Oxalsäure (L2).		
	(*c*) K_1 1,58·10^{-3}	18	$\varkappa = 2$ bis $0{,}7$	ähnl.	rel. zuv.		A6
	K_2 2,158·10^{-6}		$\mathcal{J} = 0{,}02$ bis $0{,}03$	**E2b**	Beide Kettenhälften über KCl-Brücke gegen Kalomelelektrode gemessen. Diffusionspotential berechnet. Kein NaCl-Überschuß.		
				D3			

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
					Weitere Messungen: A7; B51; B52; G2; G3; G4; H2; L2; S13; S14; S22; V2.	
23	Bernsteinsäure: $COOH{\cdot}(CH_2)_2{\cdot}COOH$					
	(*m*) K_1 $5{,}29\cdot10^{-5}$	0	$\mathcal{J} = 0{,}02$ bis $0{,}15$	**E1a**	s. zuv. bis zuv.	P9
	$5{,}46$	5				
	$5{,}70$	10				
	$5{,}88$	15				
	$6{,}07$	20				
	$6{,}21$	25				
	$6{,}34$	30				
	$6{,}45$	35				
	$6{,}50$	40				
	$6{,}51$	45				
	$6{,}52$	50				
	(*m*) K_2 $2{,}12\cdot10^{-6}$	0	$\varkappa = 0{,}5$	**E1a**	s. zuv. bis zuv.	P8
	$2{,}18$	5	$\mathcal{J} = 0{,}06$ bis $0{,}7$			
	$2{,}24$	10				
	$2{,}28$	15				
	$2{,}30$	20				
	$2{,}31$	25				
	$2{,}28$	30				
	$2{,}25$	35				
	$2{,}22$	40				
	$2{,}14$	45				
	$2{,}09$	50				
	(*m*) K_1 $6{,}89\cdot10^{-5}$	25	$\mathcal{J} = 0{,}001$ bis $0{,}01$	**E1c**	rel. zuv.	J13
	K_2 $2{,}47\cdot10^{-6}$			**R3a**	Ungenaue Rechenmethode.	
	K_1 $7{,}33\cdot10^{-5}$	50				
	K_2 $2{,}30\cdot10^{-6}$					
	K_1 $7{,}37\cdot10^{-5}$	74				
	K_2 $1{,}33\cdot10^{-6}$					

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(c) K_1 6,626·10⁻⁵	25	$\varkappa = 0{,}6$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b**	rel. zuv. Wie bei Malonsäure (J6a).	J6a
(c) K_1 6,37·10⁻⁵ K_2 2,54·10⁻⁶	25	$\mathcal{J} = 0{,}0015$ bis $0{,}006$	**E3b** **R3c** **D1**	unsicher bis rel. zuv.	G7
(c) K_1 6,41·10⁻⁵ K_2 3,33·10⁻⁶	25	$\mathcal{J} = 0{,}001$ bis $0{,}05$	**E3b** **R3b** **D1**	unsicher. Wie bei Oxalsäure (G5).	G5
(c) K_2 2,40·10⁻⁶	18	$\varkappa = 1{,}5$ bis 2 $\mathcal{J} = 0{,}012$ bis $0{,}4$	**E3a** **D2**	unsicher. Wie bei Oxalsäure (L2).	L4
(c) K_1 6,04·10⁻⁵ K_2 1,85·10⁻⁶	50	$\mathcal{J} = 0{,}025$ bis $0{,}4$	**E3a** **D1** (teilweise **D2**)	unsicher. pH-Wert der Vergleichslösung unsicher (0,01 n HCl + 0,09 n KCl); Diffusionspotentiale.	O4
(c) K_1 6,03·10⁻⁵ K_2 2,14·10⁻⁶	20	$\mathcal{J} = 0{,}0002$ bis $0{,}001$	**E3b** **R3d** **D1**	rel. zuv. bis unsicher. Mit Glaselektrode. Diffusionspotentiale.	S27
(c) K_1 6,17·10⁻⁵ K_2 2,34·10⁻⁶ K_1 6,61·10⁻⁵ K_2 2,24·10⁻⁶	18 37	$\varkappa = 1$ $\mathcal{J} = 0{,}004$ bis $0{,}1$	**E3b** **D3** **D1**	rel. zuv. Zur Berechnung von $c_{H_3O^+}$ angenommen, daß $f_{H_3O^+}$ in der Testlösung gleichen Wert hat wie in Vergleichslösung (0,001 n HCl + variable Konz. an KCl) gleicher Ionenstärke. Mit NaCl statt KCl um 5% andere Werte K erhalten. Diffusionspotentiale.	S21
(c) K_1 6,32·10⁻⁵ K_2 2,29·10⁻⁶	18	$\varkappa = 0{,}7$ bis 2 $\mathcal{J} = 0{,}004$ bis $0{,}1$	**E2b** **D3**	rel. zuv. Wie bei Fumarsäure (A7).	A7
(c) K_1 6,6·10⁻⁵ K_2 2,7·10⁻⁶	18	$\mathcal{J} = 0{,}001$ bis $0{,}01$	**E3a** **R3a** **D2**	rel. zuv. bis unsicher. pH der benützten Vergleichslösung (0,01 n HCl + 0,09 n KCl) unsicher. Diffusionspotentiale.	K28
				Weitere Messungen: A13; A14; B25a; B52; C7; D3; G2; H2; L3; M23; M24; S13; S22; S27.	

Bezeichnung III–III

No. 24–27

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
24	Glutarsäure: $COOH\text{-}(CH_2)_3\text{-}COOH$					
	(*m*) K_1 $4{,}58\cdot10^{-5}$	25	$J = 0{,}001$ bis $0{,}01$	**E1c**	rel. zuv.	
	K_2 $3{,}99\cdot10^{-6}$			**R3a**	Ungenaue Rechenmethode.	J13
	K_1 $4{,}41\cdot10^{-5}$	50				
	K_2 $4{,}34\cdot10^{-6}$					
	K_1 $3{,}69\cdot10^{-5}$	74				
	K_2 $2{,}47\cdot10^{-6}$					
	(*c*) K_1 $4{,}535\cdot10^{-5}$	25	$\varkappa = 0{,}6$	**L1**	rel. zuv.	
			$J = 0{,}0001$ bis $0{,}01$	**R1b**	Wie bei Malonsäure (J6a)	J6a
	(*c*) K_1 $4{,}46\cdot10^{-5}$	25	$J = 0{,}0015$ bis $0{,}086$	**E3b**	unsicher bis rel. zuv.	
	K_2 $3{,}77\cdot10^{-6}$			**R3c**		G7
				D1		
	(*c*) K_1 $4{,}07\cdot10^{-5}$	20	$J = 0{,}0002$ bis $0{,}001$	**E3b**	rel. zuv. bis unsicher.	
	K_2 $3{,}16\cdot10^{-6}$			**R3d**	Glaselektrode. Diffusionspotentiale.	S27
				D1		
	(*c*) K_1 $4{,}55\cdot10^{-5}$	25	$J = 0{,}001$	**E3b**	unsicher.	
	K_2 $3{,}80\cdot10^{-6}$			**R3b**	Wie bei Oxalsäure (G2).	G5
				D1		
	(*c*) K_1 $4{,}79\cdot10^{-5}$	18	$\varkappa = 0{,}7$ bis 2	**E2b**	rel. zuv.	
	K_2 $3{,}76\cdot10^{-6}$		$J = 0{,}002$ bis $0{,}1$	**D3**	Wie bei Fumarsäure (A7).	A7
					Weitere Messungen: B52; G1; G2; S13.	
25	Adipinsäure: $COOH\text{-}(CH_2)_4\text{-}COOH$					
	(*m*) K_1 $3{,}70\cdot10^{-5}$	25	$J = 0{,}001$ bis $0{,}01$	**E1c**	rel. zuv.	
	K_2 $3{,}98\cdot10^{-6}$			**R3a**	Ungenaue Rechenmethode.	J13
	K_1 $3{,}29\cdot10^{-5}$	50				
	K_2 $3{,}22\cdot10^{-6}$					
	K_1 $2{,}90\cdot10^{-5}$	74				
	K_2 $2{,}55\cdot10^{-6}$					

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(c) K_1 3,715·10^{-5}	25	$\varkappa = 0{,}6$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b**	rel. zuv. Wie bei Glutarsäure (J6a).	J6a
(c) K_1 3,82·10^{-5} K_2 3,87·10^{-6}	25	$\mathcal{J} \geq 0{,}001$	**E3b** **R3b** **D1**	unsicher. Wie bei Glutarsäure (G5).	G5
(c) K_1 3,72·10^{-5} K_2 3,80·10^{-6}	20	$\mathcal{J} = 0{,}0002$ bis $0{,}001$	**E3b** **R3d** **D1**	rel. zuv. bis unsicher. Wie bei Glutarsäure (S27).	S27
(c) K_1 4,6·10^{-5} K_2 3,6·10^{-6}	18	$\mathcal{J} = 0{,}001$ bis $0{,}01$	**E3a** **R3a** **D2**	rel. zuv. bis unsicher. Wie bei Bernsteinsäure (K28).	K28
(c) K_1 3,85·10^{-5} K_2 3,89·10^{-6}	18	$\varkappa = 0{,}7$ bis 2 $\mathcal{J} = 0{,}002$ bis $0{,}1$	**E2b** **D3**	rel. zuv. Wie bei Fumarsäure (A7).	A7
				Weitere Messungen: G2.	

26 Pimelinsäure: $COOH{\cdot}(CH_2)_5{\cdot}COOH$

(c) K_1 3,097·10^{-5}	25	$\varkappa = 0{,}6$ $\mathcal{J} = 0{,}0001$–$0{,}01$	**L1** **R1b**	rel. zuv. Wie bei Malonsäure (J6a).	J6a
(c) K_1 3,28·10^{-5} K_2 3,77·10^{-6}	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
(c) K_1 3,19·10^{-5} K_2 3,74·10^{-6}	18	$\varkappa = 0{,}7$ bis 2 $\mathcal{J} = 0{,}002$ bis $0{,}1$	**E2b** **D3**	rel. zuv. Wie bei Fumarsäure (A7).	A7
				Weitere Messungen: G2.	

27 Korksäure: $COOH{\cdot}(CH_2)_6{\cdot}COOH$

(c) K_1 2,994·10^{-5}	25	$\varkappa = 0{,}6$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b**	rel. zuv. Wie bei Malonsäure (J6a).	J6a
(c) K_1 3,04·10^{-5} K_2 3,95·10^{-6}	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
(c) K_1 3,05·10^{-5} K_2 3,85·10^{-6}	18	$\varkappa = 0{,}7$ bis 2 $\mathcal{J} = 0{,}002$ bis $0{,}9$	**E2b** **D3**	rel. zuv. Wie bei Fumarsäure (A7).	A7
				Weitere Messungen: G2; S13.	

No.	Name, Formel u. Dissoziationskonstante K	t (°C)	Bemerkungen	Methode	Kritik	Lit.
28	Azelainsäure: $COOH{\cdot}(CH_2)_7{\cdot}COOH$					
	(c) K_1 $2{,}81\cdot10^{-5}$ K_2 $3{,}85\cdot10^{-6}$	25	$\bar{f} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
	(c) K_1 $2{,}88\cdot10^{-5}$ K_2 $3{,}86\cdot10^{-6}$	18	$\varkappa = 0{,}7$ bis 2 $\bar{f} = 0{,}002$ bis 0,1	**E2b** **D3**	rel. zuv. Wie bei Fumarsäure (A7).	A7
	pK_1 4,525 pK_2 5,395	25	$\bar{f} = 0{,}005$ bis 0,1	**E3a** **D1**	rel. zuv.	S22
					Weitere Messungen: G2.	
29	Methyl-Malonsäure: $CH_3{\cdot}CH(COOH)_2$					
	(m) K_1 $7{,}59\cdot10^{-4}$ K_2 $1{,}35\cdot10^{-6}$	20	$\bar{f} = 0{,}01$ u. 0,003	**E3b** **D1**	unsicher. Konzentrationen für Berechnung der f nach D.H.-Gl. zu hoch. Diffusionspotentiale.	S14
	(c) K_1 $8{,}92\cdot10^{-4}$ K_2 $1{,}75\cdot10^{-6}$	25	$\bar{f} = 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
	(c) K_1 $8{,}47\cdot10^{-4}$	25	$\varkappa = 0{,}7$ $\bar{f} = 0{,}0001$ bis 0,01	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J7
					Weitere Messungen: G4; V2.	
30	Äthyl-Malonsäure: $CH_3{\cdot}CH_2{\cdot}CH(COOH)_2$					
	(c) K_1 $1{,}094\cdot10^{-3}$	25	$\varkappa = 0{,}7$ $\bar{f} = 0{,}0001$ bis 0,01	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J7
	(c) K_1 $1{,}03\cdot10^{-3}$ K_2 $1{,}47\cdot10^{-6}$	25	$\bar{f} \geq 0{,}001$	**E3b** **D1** **R3b**	unsicher. Wie bei Oxalsäure (G5)	G5
					Weitere Messungen: G4; S14; V2.	

31 n-Propyl-Malonsäure: $CH_3{\cdot}(CH_2)_2{\cdot}CH(COOH)_2$

(c) K_1	$1{,}026{\cdot}10^{-3}$	25	$\varkappa = 0{,}7$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J7
(c) K_1	$1{,}01{\cdot}10^{-3}$	25	$\mathcal{J} \geq 0{,}001$	**E3b**	unsicher.	G5
K_2	$1{,}43{\cdot}10^{-6}$			**D1 R3b**	Wie bei Oxalsäure (G5).	
					Weitere Messungen: G4; S14.	

32 iso-Propyl-Malonsäure: $(CH_3)_2CH{\cdot}CH(COOH)_2$

(c) K_1	$1{,}14{\cdot}10^{-3}$	25	$\mathcal{J} \geq 0{,}001$	**E3b**	unsicher.	G5
K_2	$1{,}32{\cdot}10^{-6}$			**D1 R3b**	Wie bei Oxalsäure (G5).	
					Weitere Messungen: G4.	

33 Dimethyl-Malonsäure: $(CH_3)_2C(COOH)_2$

(c) K_1	$7{,}06{\cdot}10^{-4}$	25	$\varkappa = 0{,}7$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6b).	J7
(c) K_1	$6{,}83{\cdot}10^{-4}$	25	$\mathcal{J} \geq 0{,}001$	**E3b**	unsicher.	G5
K_2	$8{,}72{\cdot}10^{-7}$			**D1 R3b**	Wie bei Oxalsäure (G5).	
					Weitere Messungen: G4; S14; V2.	

34 Methyl-Äthyl-Malonsäure: $CH_3{\cdot}CH_2{\cdot}C(CH_3)(COOH)_2$

(c) K_1	$1{,}543{\cdot}10^{-3}$	25	$\varkappa = 0{,}7$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J7
(c) K_1	$1{,}38{\cdot}10^{-3}$	25	$\mathcal{J} \geq 0{,}001$	**E3b**	unsicher.	G5
K_2	$3{,}86{\cdot}10^{-7}$			**D1 R3b**	Wie bei Oxalsäure (G5).	
					Weitere Messungen: G4; V2.	

35 Diäthyl-Malonsäure: $(CH_3{\cdot}CH_2)_2C(COOH)_2$

(c) K_1	$7{,}08{\cdot}10^{-3}$	25	$\varkappa = 0{,}7$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J7

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
	(c) K_1 6,15·10^{-3} K_2 5,1·10^{-8}	25	$J \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
					Weitere Messungen: G4; S14; V2.	
36	Äthyl-n-Propyl-Malonsäure: $CH_3{\cdot}(CH_2)_2{\cdot}C(CH_2{\cdot}CH_3)(COOH)_2$					
	(c) K_1 7,837·10^{-3}	25	$\varkappa = 0{,}7$ $J = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J7
	(c) K_1 7,16·10^{-3} K_2 3,7·10^{-8}	25	$J \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
					Weitere Messungen: V2.	
37	Di-n-propyl-Malonsäure: $(CH_3{\cdot}CH_2{\cdot}CH_2)_2C(COOH)_2$					
	(c) K_1 9,198·10^{-3}	25	$\varkappa = 0{,}7$ $J = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J7
	(c) K_1 3,58·10^{-3} K_2 3,1·10^{-8}	25	$J \geq 0{,}001$	**E3b** **D1 R3b**	unsicher.	G5
					Weitere Messungen: G4; S14; V2.	
38	Brenzweinsäure (Methyl-Bernsteinsäure): $COOH{\cdot}CH(CH_3){\cdot}CH_2{\cdot}COOH$					
	(c) K_2 2,33·10^{-6}	18	$\varkappa = 1{,}5$ bis 2 $J = 0{,}02$ bis $0{,}12$	**E2b** **D2**	unsicher. Wie bei Oxalsäure (L2).	L4
39	*meso*-α,α'-Dimethyl-Bernsteinsäure: Smp. 209°C. $COOH{\cdot}CH(CH_3){\cdot}CH(CH_3){\cdot}COOH$					
	(c) K_1 1,70·10^{-4} K_2 1,16·10^{-6}	25	$J \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5

40	*rac.*-α,α'-Dimethyl-Bernsteinsäure: Smp. 129 C. $COOH{\cdot}CH(CH_3){\cdot}CH(CH_3){\cdot}COOH$					
	(*c*) K_1 $1{,}15{\cdot}10^{-4}$ K_2 $6{,}36{\cdot}10^{-7}$	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5)	G5
41	Äthyl-Bernsteinsäure: $COOH{\cdot}CH(CH_2{\cdot}CH_3){\cdot}CH_2{\cdot}COOH$					
	(*c*) K_1 $8{,}3{\cdot}10^{-5}$	25	$c = 0{,}0005$ bis $0{,}03$	Leitf.	Experimentelle Originalarbeit nicht zugänglich gewesen (H25).	H26
42	α,α-Diäthyl-Bernsteinsäure: $COOH{\cdot}C(CH_2{\cdot}CH_3)_2{\cdot}CH_2{\cdot}COOH$					
	(*c*) K_1 $1{,}44{\cdot}10^{-4}$	25	$c = 0{,}001$ bis $0{,}03$	Leitf.	Wie bei Äthyl-Bernsteinsäure (H26).	H26
43	*meso*-α,α'-Diäthyl-Bernsteinsäure: Smp. 192°C. $COOH{\cdot}CH(CH_2{\cdot}CH_3){\cdot}CH(CH_2{\cdot}CH_3){\cdot}COOH$					
	(*c*) K_1 $2{,}33{\cdot}10^{-4}$ K_2 $3{,}47{\cdot}10^{-7}$	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
	(*c*) K_1 $2{,}32{\cdot}10^{-4}$	25	$c = 0{,}0005$ bis $0{,}02$	Leitf.	Wie bei Äthyl-Bernsteinsäure (H26).	H26
44	*rac.*-α,α'-Diäthyl-Bernsteinsäure: Smp. 129°C. $COOH{\cdot}CH(CH_2{\cdot}CH_3){\cdot}CH(CH_2{\cdot}CH_3){\cdot}COOH$					
	(*c*) K_1 $3{,}11{\cdot}10^{-4}$ K_2 $2{,}54{\cdot}10^{-7}$	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
	(*c*) K_1 $3{,}43{\cdot}10^{-4}$	25	$c = 0{,}0005$ bis $0{,}03$	Leitf.	Wie bei Äthyl-Bernsteinsäure (H26).	H26
45	Triäthyl-Bernsteinsäure: $COOH{\cdot}CH(CH_2{\cdot}CH_3){\cdot}C(CH_2{\cdot}CH_3)_2{\cdot}COOH$					
	(*c*) K_1 $1{,}83{\cdot}10^{-3}$	25	$c = 0{,}0006$ bis $0{,}02$	Leitf.	Wie bei Äthyl-Bernsteinsäure (H26).	H26
46	Tetramethyl-Bernsteinsäure: $COOH{\cdot}C(CH_3)_2{\cdot}C(CH_3)_2{\cdot}COOH$					
	(*c*) K_1 $3{,}19{\cdot}10^{-4}$ (*c*) K_2 $5{,}2{\cdot}10^{-8}$	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
47	β-Methyl-Glutarsäure: $COOH{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}COOH$					
	(*m*) K_1 $5{,}61{\cdot}10^{-5}$ K_2 $3{,}91{\cdot}10^{-6}$	25	$\mathcal{J} = 0{,}001$ bis $0{,}01$	**E1c** **R3a**	rel. zuv. Ungenaue Rechenmethode.	J13
	K_1 $5{,}17{\cdot}10^{-5}$ K_2 $3{,}18{\cdot}10^{-6}$	50				
	K_1 $4{,}29{\cdot}10^{-5}$ K_2 $2{,}23{\cdot}10^{-6}$	74				

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
	(c) K_1 $5{,}65\cdot10^{-5}$ K_2 $5{,}96\cdot10^{-8}$	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5). Über die Größenordnung von K_2 vergl. (I1).	G5
	(c) K_1 $5{,}815\cdot10^{-5}$	25	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J8
					Weitere Messungen: G1.	
48	*β*-Äthyl-Glutarsäure: $COOH{\cdot}CH_2{\cdot}CH(CH_2{\cdot}CH_3){\cdot}CH_2{\cdot}COOH$					
	(c) K_1 $5{,}17\cdot10^{-5}$ K_2 $4{,}69\cdot10^{-8}$	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5). Über die Größenordnung von K_2 vergl. (I1).	G5
	(c) K_1 $5{,}139\cdot10^{-5}$	25	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J8
49	*β*,*β*-Dimethyl-Glutarsäure: $COOH{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}COOH$					
	(m) K_1 $2{,}01\cdot10^{-4}$ K_2 $4{,}57\cdot10^{-7}$	25	$\mathcal{J} = 0{,}001$ bis $0{,}01$	**E1c** **R3a**	rel. zuv. Ungenaue Rechenmethode.	J13
	K_1 $1{,}28\cdot10^{-4}$ K_2 $3{,}26\cdot10^{-7}$	50				
	K_1 $9{,}33\cdot10^{-5}$ K_2 $2{,}52\cdot10^{-7}$	74				
	(c) K_1 $1{,}903\cdot10^{-4}$	25	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J8
	(c) K_1 $1{,}98\cdot10^{-4}$ K_2 $5{,}10\cdot10^{-7}$	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
					Weitere Messungen: G1.	

50	β-n-Propyl-Glutarsäure: $CH_3{\cdot}(CH_2)_2{\cdot}CH(CH_2{\cdot}COOH)_2$					
	(*c*) K_1 4,910·10^{-5}	25	$\varkappa = 0{,}8$ $\mathcal{J} = 0{,}0001$ bis 0,01	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J8
	(*c*) K_1 4,87·10^{-5} K_2 4,11·10^{-6}	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5). Über die Großenordnung von K_2 vergl. (H).	G5
					Weitere Messungen: G1.	
51	β-iso-Propyl-Glutarsäure: $(CH_3)_2CH{\cdot}CH(CH_2{\cdot}COOH)_2$					
	(*m*) K_1 5,05·10^{-5} K_2 3,08·10^{-6}	25	$\mathcal{J} = 0{,}001$ bis 0,01	**E1c** **R3a**	rel. zuv. Ungenaue Rechenmethode.	J13
	K_1 4,63·10^{-5} K_2 2,37·10^{-6}	50				
	K_1 3,87·10^{-5} K_2 1,67·10^{-6}	74				
52	β,β-Methyl-Äthyl-Glutarsäure: $CH_3{\cdot}CH_2{\cdot}C(CH_3)(CH_2{\cdot}COOH)_2$					
	(*c*) K_1 2,335·10^{-4}	25	$\varkappa = 0{,}8$ $\mathcal{J} = 0{,}0001$ bis 0,01	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J8
	(*c*) K_1 2,40·10^{-4} K_2 2,00·10^{-7}	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
53	β,β-Diäthyl-Glutarsäure: $(CH_3{\cdot}CH_2)_2C(CH_2{\cdot}COOH)_2$					
	(*c*) K_1 3,286·10^{-4}	25	$\varkappa = 0{,}8$ $\mathcal{J} = 0{,}0001$ bis 0,01	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J8
	(*c*) K_1 2,38·10^{-4} K_2 7,5·10^{-8}	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
					Weitere Messungen: G1.	
54	β,β-Methyl-n-Propyl-Glutarsäure: $CH_3{\cdot}(CH_2)_2{\cdot}C(CH_3)(CH_2{\cdot}COOH)_2$					
	(*c*) K_1 2,367·10^{-4}	25	$\varkappa = 0{,}8$ $\mathcal{J} = 0{,}0001$ bis 0,01	**L1** **R1b** **K1c**	rel. zuv. Wie bei Malonsäure (J6a).	J8

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
55	β,β-Äthyl-n-Propyl-Glutarsäure: $CH_3{\cdot}(CH_2)_2{\cdot}C(CH_2{\cdot}CH_3)(CH_2{\cdot}COOH)_2$					
	(c) K_1 $3{,}086{\cdot}10^{-4}$	25	$\varkappa = 0{,}8$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K1c**	unsicher. Wie bei Malonsäure (J6a). Wegen geringer Loslichkeit nur wenige Meßpunkte bei sehr kleinen Konzentrationen.	J8
56	β,β-Di-n-propyl-Glutarsäure: $(CH_3{\cdot}CH_2{\cdot}CH_2)_2C(CH_2{\cdot}COOH)_2$					
	(c) K_1 $2{,}05{\cdot}10^{-4}$ K_2 $4{,}9{\cdot}10^{-8}$	25	$\mathcal{J} \geq 0{,}001$	**E3b** **D1 R3b**	unsicher. Wie bei Oxalsäure (G5).	G5
					Weitere Messungen: G1.	
			112			
57	Acrylsäure: $CH_2{:}CH{\cdot}COOH$					
	$5{,}66{\cdot}10^{-5}$	25	$\mathcal{J} = 0{,}1$ bis $0{,}5$	**E2c**	rel. zuv.	K11
	$5{,}56{\cdot}10^{-5}$	25	$\varkappa = 1$ $\varepsilon = 0{,}001$ bis $0{,}013$	**L1** **R1a** **K2e**	rel. zuv. Solvens- u. Hydrolysekorr. unsicher.	D13
	$5{,}50{\cdot}10^{-5}$	25	$\varkappa = 0{,}6$ bis $0{,}8$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** ähnl. **R1b** **K1c**	rel. zuv. J_0 Wert fraglich.	G9
	$5{,}52{\cdot}10^{-5}$	25	$\varepsilon = 0{,}005$	**E3a** **D1**	rel. zuv.	G9
					Weitere Messungen: 12.	
58	*trans*-Crotonsäure: $CH_3{\cdot}CH$ $\|$ $HC{\cdot}COOH$					
	$1{,}95{\cdot}10^{-5}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	L11

	$1{,}975 \cdot 10^{-5}$	25	$\varkappa = 1$ $\mathcal{J} = 0{,}0002$ bis $0{,}03$	**L1** **K1a** **R1b**	zuv.	S8
	$2{,}03 \cdot 10^{-5}$	25	$\varkappa = 0{,}4$ $c = 0{,}0004$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	I3
	$2{,}03 \cdot 10^{-5}$	25	$\varkappa = 0{,}6$ bis $0{,}8$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** ähnl. **R1b** **K1c**	rel. zuv.	G9
	$2{,}10 \cdot 10^{-5}$	25	$c = 0{,}005$	**E3a** **D1**	rel. zuv.	V4
59	*cis*-Crotonsäure (Isocrotonsäure): $HC \cdot CH_3$ $\parallel$ $HC \cdot COOH$					
	$3{,}9 \cdot 10^{-5}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	L8
60	Vinyl-Essigsäure: $CH_2{:}CH \cdot CH_2 \cdot COOH$					
	$4{,}62 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}001$ bis $0{,}012$	**L1** **R1a** **K2e**	rel. zuv.	D13
	$4{,}8 \cdot 10^{-5}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	rel. zuv.	L8
	$4{,}48 \cdot 10^{-5}$	25	$\varkappa = 0{,}4$ $c = 0{,}0005$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	I3
	$4{,}445 \cdot 10^{-5}$	25	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}0004$ bis $0{,}003$	**L1** ähnl. **R1c** **K1d**	zuv.	I2
61	α-Methacrylsäure: $CH_2{:}C(CH_3) \cdot COOH$					
	$2{,}2 \cdot 10^{-5}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	L8

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No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
62	Tetrolsäure; $CH_3{-}C{\equiv}C{-}COOH$					
	$1{,}85 \cdot 10^{-4}$	18	$\varkappa = 0{,}3$ $\gamma = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	13
	$2{,}22 \cdot 10^{-4}$	25	$\varkappa = 0{,}7$ $\gamma = 0{,}0001$ bis $0{,}01$	**L1** ähnl. **R1a** **K1c**	rel. zuv.	69
	$2{,}22 \cdot 10^{-4}$	25	$\epsilon = 0{,}005$	**E3a** **D1**	rel. zuv.	69
63	n-Buten-1-carbonsäure-1 (β-Allyl-Acrylsäure); $CH_2{=}CH{-}CH_2{-}CH_2{-}COOH$					
	$2{,}02 \cdot 10^{-5}$	25	$\varkappa = 0{,}4$ $\epsilon = 0{,}0002$ bis $0{,}014$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13
64	n-Buten-2-carbonsäure-1; $CH_3{-}CH_2{-}CH{=}CH_2{-}COOH$					
	$3{,}11 \cdot 10^{-5}$	25	$\varkappa = 0{,}4$ $\epsilon = 0{,}00015$ bis $0{,}013$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13
65	n-Buten-3-carbonsäure-1 (Allyl-Essigsäure); $CH_2{=}CH{-}CH_2{-}CH_2{-}COOH$					
	$2{,}0 \cdot 10^{-5}$	18	$\varkappa = 0{,}9$ $\gamma = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	13
	$2{,}115 \cdot 10^{-5}$	25	$\varkappa = 1$ $\epsilon = 0{,}002$ bis $0{,}017$	**L1** **R1a** **K2c**	rel. zuv.	D13
	$2{,}10 \cdot 10^{-5}$	25	$\varkappa = 0{,}4$ $\epsilon = 0{,}0003$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13

66	Angelicasäure: $HC{\cdot}CH_3$ ‖ $CH_3{\cdot}C{\cdot}COOH$					
	$5{,}1{\cdot}10^{-5}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	LB
67	Tiglinsäure: $CH_3{\cdot}CH$ ‖ $CH_3{\cdot}C{\cdot}COOH$					
	$1{,}1{\cdot}10^{-5}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	LB
68	β,β-Dimethyl-Acrylsäure: $(CH_3)_2C{:}CH{\cdot}COOH$					
	$7{,}3{\cdot}10^{-6}$	18	$\varkappa = 0{,}3$ $\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	LB
	$7{,}6{\cdot}10^{-6}$	25	$\varkappa = 0{,}4$ $c = 0{,}0004$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13
	$7{,}569{\cdot}10^{-6}$	25	$\varkappa = 0{,}7$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**L1** ähnl. **R1b** **K1c**	rel. zuv.	G9
	$7{,}62{\cdot}10^{-6}$	25	$c = 0{,}005$	**E3a** **D1**	rel. zuv.	G9
69	n-Penten-1-carbonsäure-1: $CH_3{\cdot}(CH_2)_2{\cdot}CH{:}CH{\cdot}COOH$					
	$1{,}98{\cdot}10^{-5}$	25	$\varkappa = 0{,}4$ $c = 0{,}0003$ bis $0{,}008$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13
70	n-Penten-2-carbonsäure-1: $CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$					
	$3{,}05{\cdot}10^{-5}$	25	$\varkappa = 0{,}4$ $c = 0{,}0003$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
71	n-Penten-3-carbonsäure-1: $CH_3{\cdot}CH{:}CH{\cdot}(CH_2)_2{\cdot}COOH$					
	$1{,}91{\cdot}10^{-5}$	25	$\varkappa = 0{,}4$ $c = 0{,}0006$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13
72	n-Penten-4-carbonsäure-1: $CH_2{:}CH{\cdot}(CH_2)_2{\cdot}COOH$					
	$1{,}90{\cdot}10^{-5}$	25	$\varkappa = 0{,}4$ $c = 0{,}0006$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13
73	*trans*-2-Methyl-n-Buten-1-carbonsäure-1: $CH_3{\cdot}CH_2{\cdot}C(CH_3){:}CH{\cdot}COOH$					
	$7{,}4{\cdot}10^{-6}$	25	$\varkappa = 0{,}4$ $c = 0{,}0005$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13
74	*cis*-2-Methyl-n-Buten-1-carbonsäure: $CH_3{\cdot}CH_2{\cdot}C(CH_3){:}CH{\cdot}COOH$					
	$7{,}1{\cdot}10^{-6}$	25	$\varkappa = 0{,}4$ $c = 0{,}0006$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13
75	3-Methyl-n-Buten-1-carbonsäure-1 (iso-Propyl-Acrylsäure): $CH_2{\cdot}CH(CH_3){\cdot}CH{:}CH{:}COOH$					
	$1{,}99{\cdot}10^{-5}$	25	$\varkappa = 0{,}4$ $c = 0{,}0003$ bis $0{,}01$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13
76	3-Methyl-n-Buten-2-carbonsäure-1: $CH_3{\cdot}C(CH_3){:}CH{\cdot}CH_2{\cdot}COOH$					
	2,51	25	$\varkappa = 0{,}4$ $c = 0{,}002$ bis $0{,}013$	**L1** ähnl. **R1a** **K1d**	rel. zuv.	13

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77	4-Methyl-n-Penten-3-carbonsäure-1: $CH_2{\cdot}C(CH_3){:}CH{\cdot}(CH_2)_2{\cdot}COOH$					
	$1{,}59{\cdot}10^{-5}$	25	$\varkappa = 0{,}4$ c=0,0007 bis 0,015	**L1** ähnl. **R1a** **K1d**	rel. zuv.	I3
78	Maleinsäure: $\begin{matrix}HC{\cdot}COOH\\ \|\\ HC{\cdot}COOH\end{matrix}$					
	K_1 $1{,}00{\cdot}10^{-2}$ K_2 $5{,}50{\cdot}10^{-7}$	25	$\varkappa = 0{,}1$ $\mathcal{J} = 0{,}004$ bis 0,03	**E3b** **D3**	rel. zuv.	S21
	K_1 $1{,}02{\cdot}10^{-2}$ K_2 $4{,}79{\cdot}10^{-7}$	37				
	K_1 $1{,}24{\cdot}10^{-2}$ K_2 $5{,}38{\cdot}10^{-7}$	18	$\varkappa = 0{,}7$ bis 2 $\mathcal{J} = 0{,}004$ bis 0,1	**E2b** **D3**	rel. zuv.	A7
	K_1 $1{,}14{\cdot}10^{-2}$ K_2 $5{,}95{\cdot}10^{-7}$	25	$\varkappa = 0{,}8$ $\mathcal{J} = 0{,}004$ bis 0,007	**L1**, **R1b** und **K1c** und **E3b**, **D1** **R3c**	rel. zuv.	G11
	K_2 $5{,}1{\cdot}10^{-7}$	18	$\varkappa = 1{,}5$ bis 2 $\mathcal{J} = 0{,}004$ bis 0,5	**E3a** **D2**	unsicher.	L2
					Weitere Messungen: A13; B51; C7; V5.	
79	Fumarsäure: $\begin{matrix}HOOC{\cdot}CH\\ \|\\ HC{\cdot}COOH\end{matrix}$					
	K_1 $9{,}57{\cdot}10^{-4}$ K_2 $3{,}51{\cdot}10^{-5}$	18	$\varkappa = 0{,}7$ bis 2 $\mathcal{J} = 0{,}04$ bis 0,1	**E2b** **D3**	rel. zuv.	A7
	K_1 $9{,}57{\cdot}10^{-4}$ K_2 $4{,}13{\cdot}10^{-5}$	25	$\varkappa = 0{,}8$ $\mathcal{J} = 0{,}002$ bis 0,007	**E3b** **D1, R3c**	rel. zuv.	G11
	K_1 $9{,}311{\cdot}10^{-4}$ K_2 $3{,}420{\cdot}10^{-5}$	18	$\varkappa = 0{,}1$ $\mathcal{J} = 0{,}004$ bis 0,03	**E3b** **D3** **D1**	rel. zuv.	S21
	K_1 $9{,}078{\cdot}10^{-4}$ K_2 $3{,}083{\cdot}10^{-5}$	37				
	K_2 $3{,}37{\cdot}10^{-5}$	18	$\varkappa = 1{,}5$ bis 2 $\mathcal{J} = 0{,}01$ bis 0,4	**E3a** **D2**	unsicher. $\log f_\pm = A\sqrt{\mathcal{J}}$.	L4
					Weitere Messungen: A13; B51; C7; L3; V5.	

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
80	Glutaconsäure: $COOH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COOH$					
	K_1 $1{,}711{\cdot}10^{-4}$	25	$\varkappa = 0{,}7$ $c = 0{,}001$ bis $0{,}01$	**L1, R1b** **K1c** **K1d**	rel. zuv.	G9
	K_1 $1{,}70{\cdot}10^{-4}$ K_2 $8{,}38{\cdot}10^{-6}$	25	$c = 0{,}005$	**E3a** **D1**	rel. zuv.	G9
	K_1 $1{,}70{\cdot}10^{-4}$ K_2 $8{,}38{\cdot}10^{-6}$	25	$c = 0{,}005$	**L1** **E3b** **D1**	rel. zuv.	V5
81	Citraconsäure: $CH_3{\cdot}C(COOH){=}HC{\cdot}COOH$					
	K_2 $6{,}8{\cdot}10^{-7}$	18	$\varkappa = 1{,}5$ bis 2 $\mathcal{J} = 0{,}017$ bis $0{,}4$	**E3a** **D2**	unsicher.	L2
					Weitere Messungen: A13.	
82	Mesaconsäure: $HOOC{\cdot}C(CH_3){=}HC{\cdot}COOH$					
	K_2 $1{,}5{\cdot}10^{-5}$	18	$\varkappa = 1{,}5$ bis 2 $\mathcal{J} = 0{,}017$ bis $0{,}4$	**E3a** **D2**	unsicher.	L2
					Weitere Messungen: A13.	
83	Itaconsäure: $CH_2{:}C(COOH){\cdot}CH_2{\cdot}COOH$					
	K_2 $2{,}9{\cdot}10^{-6}$	18	$\varkappa = 1{,}5$ bis 2 $\mathcal{J} = 0{,}017$ bis $0{,}4$	**E3a** **D2**	unsicher.	L2
					Weitere Messungen: A13.	

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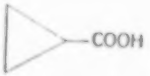
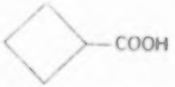
84 Cyclopropan-carbonsäure:



(c)	$1{,}49 \cdot 10^{-5}$	25	$J = 0{,}1$ bis $0{,}5$	**E2c**	rel. zuv. bis unsicher. Wie bei Acrylsäure (K11).

K11

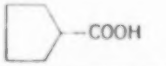
85 Cyclobutan-carbonsäure:



(c)	$1{,}64 \cdot 10^{-5}$	25	$J = 0{,}1$ bis $0{,}5$	**E2c**	rel. zuv. bis unsicher Wie bei Acrylsäure (K11).

K11

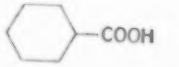
86 Cyclopentan-carbonsäure:



(c)	$1{,}03 \cdot 10^{-5}$	25	$J = 0{,}1$ bis $0{,}5$	**E2c**	rel. zuv. bis unsicher. Wie bei Acrylsäure (K11).

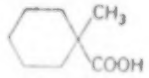
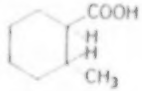
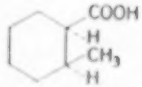
K11

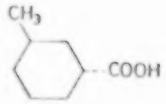
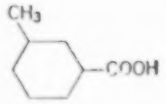
87 Cyclohexan-carbonsäure:

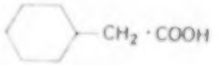
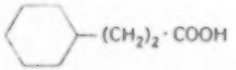


(c)	$1{,}26 \cdot 10^{-5}$(1) $1{,}22 \cdot 10^{-5}$(2)	25	$J = 0{,}05$ bis $3{,}0$	**E2b** **E2c**	rel. zuv. Messungen gegen HCl stimmen überein mit denen gegen Benzoesäure bzw. Essigsäure. Wert (1) nach Meth. **E2c** gegen Benzoesäure, Wert (2) gegen Essigsäure gemessen. Unsicherheiten in der Extrapolation auf $J=0$ wegen rel. hoher Ionenstärken. Der Wert (2) ist vorzuziehen, weil er mit K für Essigsäure berechnet wurde, das sicherer bekannt ist als K für Benzoesäure.

K8

No.	*Name, Formel u. Dissoziationskonstante k*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	(*c*) $1{,}26 \cdot 10^{-5}$	25	$\varkappa = 0{,}6$ $c = 0{,}0002$ bis $0{,}004$	**L1** **R1a** **K2e**	rel. zuv. Glaszellen, Wasserthermostat. Unsichere Solvenskorr. Salzlosungen enthielten Überschuß an Saure (0,2%) der nicht berücksichtigt wurde.	D11
88	1-Methyl-Cyclohexan-carbonsäure: 					
	(*c*) $7{,}39 \cdot 10^{-5}$	25	$\varkappa = 0{,}6$ $c = 0{,}0005$ bis $0{,}002$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Cyclohexan-carbonsäure (D11).	D11
89	*trans*-2-Methyl-Cyclohexan-carbonsäure: 					
	(*c*) $1{,}84 \cdot 10^{-6}$	25	$\varkappa = 0{,}6$ $c = 0{,}0005$ bis $0{,}003$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Cyclohexan-carbonsäure (D11).	D11
90	*cis*-2-Methyl-Cyclohexan-carbonsäure: 					

	(*c*) $9{,}21 \cdot 10^{-6}$	25	$\varkappa = 0{,}6$ $c = 0{,}0005$ bis $0{,}004$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Cyclohexan-carbonsäure (D11).	D11
91	*trans*-3-Methyl-Cyclohexan-carbonsäure: 					
	(*c*) $9{,}5 \cdot 10^{-6}$	25	$\varkappa = 0{,}6$ $c = 0{,}0002$ bis $0{,}001$	**L1** **R1a** **K2e**	unsicher. Es wurden *K*-Werte für ein Gemisch aus *cis*- und *trans*-Form (1:1) gemessen, daraus der Wert 9,5 geschätzt. Weiter wie bei Cyclohexan-carbonsäure (D11).	D11
	(*c*) $2{,}7 \cdot 10^{-5}$	25		**L**	unsicher. Ohne experimentelle Angaben.	M28
92	*cis*-3-Methyl-Cyclohexan-carbonsäure: 					
	(*c*) $1{,}31 \cdot 10^{-5}$	25	$\varkappa = 0{,}6$ $c = 0{,}00015$ bis $0{,}0017$	**L1** **R1a** **K2e**	unsicher. Wie bei Cyclohexan-carbonsäure (D11).	D11
	(*c*) $2{,}4 \cdot 10^{-5}$	25		**L**	unsicher. Ohne experimentelle Angaben.	M28
93	*trans*-4-Methyl-Cyclohexan-carbonsäure:					

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
	(c) $1{,}30 \cdot 10^{-5}$	25	$\varkappa = 0{,}6$ $c = 0{,}0004$ bis $0{,}003$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Cyclohexan-carbonsäure.	D11
94	*cis*-4-Methyl-Cyclohexan-carbonsäure:					
	(c) $9{,}2 \cdot 10^{-6}$	25	$\varkappa = 0{,}6$ $c = 0{,}0003$ bis $0{,}002$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Cyclohexan-carbonsäure (D11).	D11
95	Cyclohexyl-Essigsäure: 					
	(c) $1{,}58 \cdot 10^{-5}$			**L1**	unsicher. Wenig experim. Angaben; keine Aktivitätskoeff. berücksichtigt.	C15
96	Cyclohexyl-Propionsäure: 					
	(c) $1{,}23 \cdot 10^{-5}$			**L1**	unsicher. Wenig experim. Angaben; keine Aktivitätskoeff. berücksichtigt.	C15

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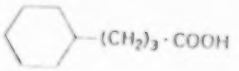
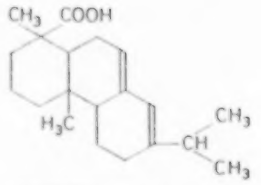
97 Cyclohexyl-n-Buttersäure:



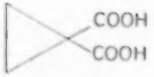
(c) $1{,}12 \cdot 10^{-5}$			**L1**	unsicher. Wenig experim. Angaben; keine Aktivitätskoeff. berücksichtigt.	G15

98 Abietinsäure:



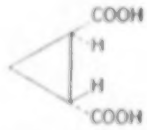
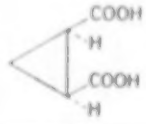
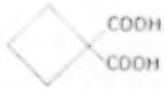
pK 7,62	fehlt		**E3b** **D1**	unsicher.	B1

99 Cyclopropan-1,1-dicarbonsäure:

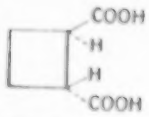


K_1 $1{,}50 \cdot 10^{-2}$ K_2 $3{,}71 \cdot 10^{-6}$	25	$\varkappa = 0{,}6$ bis $0{,}8$ $\bar{J} = 0{,}0001$ bis $0{,}01$	**E3b** **D1** **R3b** für K_1 auch **L1**, **R1b**	rel. zuv.	G8

Weitere Messung: V3.

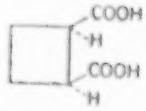
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
100	*trans*-Cyclopropan-1,2-dicarbonsäure: 					
	K_1 2,24·10^{-3}	24	$\varkappa = 3$	**E3a**	unsicher.	W4
	K_2 7,41·10^{-6}		$\bar{\gamma} = 0{,}12$	**D1**	$\log f = .1^2\,\bar{\gamma}$.	
101	*cis*-Cyclopropan-1,2-dicarbonsäure: 					
	K_1 4,68·10^{-4}	24	$\varkappa = 3$	**E3a**	unsicher.	W5
	K_2 3,39·10^{-7}	25	$\bar{\gamma} = 0{,}12$	**D1**		
102	Cyclobutan-1,1-dicarbonsäure: 					
	K_1 7,47·10^{-4}	25	$\varkappa = 0{,}6$ bis $0{,}8$	**E3b**	rel. zuv.	GB
	K_2 1,32·10^{-6}		$\bar{\gamma} = 0{,}0001$ bis $0{,}01$	**D1** **R3b** für K_1 auch **L1, R1b**		
					Weitere Messung: V3.	

103 *trans*-Cyclobutan-1,2-dicarbonsäure:



K_1 1,62·10⁻³	19	$\varkappa = 3$	**E3a**	unsicher.	K42
K_2 2,46·10⁻⁶	20	$\mathcal{J} \geqslant 0{,}12$	**D1**	Wie Terephthalsäure (K40).	

104 *cis*-Cyclobutan-1,2-dicarbonsäure:



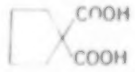
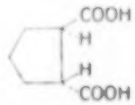
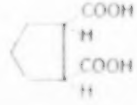
K_1 1,26·10⁻³	19	$\varkappa = 3$	**E3a**	unsicher.	K42
K_2 1,29·10⁻⁶	18	$\mathcal{J} \geqslant 0{,}12$	**D1**	Wie Terephthalsäure (K40).	

105 *trans*-Cyclobutan-1,3-dicarbonsäure:

K_1 1,55·10⁻³	25	$\varkappa = 3$	**E3a**	unsicher.	W4
K_2 5,25·10⁻⁶		$\mathcal{J} \geqslant 0{,}12$	**D1**		

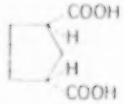
106 *cis*-Cyclobutan-1,3-dicarbonsäure:

K_1 9,33·10⁻⁵	25	$\varkappa = 3$	**E3a**	unsicher.	W5
K_2 4,90·10⁻⁶		$\mathcal{J} \geqslant 0{,}12$	**D1**		

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
107	Cyclopentan-1,1-dicarbonsäure: 					
	K_1 5,89·10^{-4} K_2 8,3·10^{-6}	25	$\varkappa = 0{,}6$ bis 0,8 $\bar{f} = 0{,}0001$ bis 0,01	**E3b**, **D1**, **R3b** K_1 auch **L1**, **R1b**	rel. zuv.	GB
					Weitere Messung: V3.	
108	*trans*-Cyclopentan-1,2-dicarbonsäure: 					
	K_1 1,1·10^{-4} K_2 1,4·10^{-6}	25	$c = 0{,}001$ bis 0,005	**E3b** **D1**	unsicher.	H
	K_1 1,39·10^{-4} K_2 1,23·10^{-6}	18	$\varkappa = 3$ $\bar{f} \geqslant 0{,}12$	**E3a** **D1**	unsicher. $\log f = A\sqrt{\bar{f}}$.	W4
109	*cis*-Cyclopentan-1,2-dicarbonsäure: 					

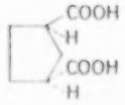
K_1 3,7·10^{-5} K_2 2,7·10^{-7}	25	c = 0,001 bis 0,005	**E3b** **D1**	unsicher.	11
K_1 4,27·10^{-5} K_2 3,09·10^{-7}	19	$\varkappa = 3$ $J \geq 0{,}12$	**E3a** **D1**	unsicher.	W5

110 *trans*-Cyclopentan-1,3-dicarbonsäure:



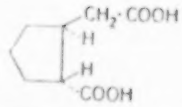
K_1 4,8·10^{-5} K_2 3,8·10^{-6}	25	c = 0,001 bis 0,005	**E3b** **D1**	unsicher.	11
K_1 3,98·10^{-5} K_2 3,55·10^{-6}	22	$\varkappa = 3$ $J \geq 0{,}12$	**E3a** **D1**	unsicher.	W4

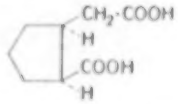
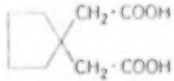
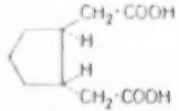
111 *cis*-Cyclopentan-1,3-dicarbonsäure:

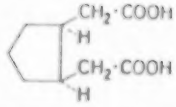
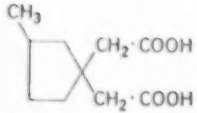
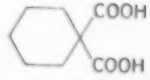


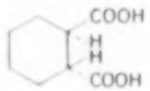
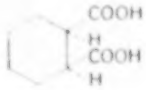
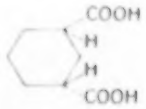
K_1 5,5·10^{-5} K_2 3,1·10^{-6}	25	c = 0,001 bis 0,005	**E3b** **D1**	unsicher.	11
K_1 5,89·10^{-5} K_2 2,95·10^{-6}	21	$\varkappa = 3$ $J \geq 0{,}12$	**E3a** **D1**	unsicher.	W5

112 *trans*-Cyclopentan-1-carbonsäure-2-Essigsäure:

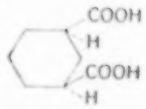


No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	K_1 4,07·10^{-3} K_2 2,14·10^{-6}	20		**E3b** **D1** **R3d**	unsicher. Wenig exper. Angaben.	S28
113	*cis*-Cyclopentan-1-carbonsäure-2-Essigsäure: 					
	K_1 3,98·10^{-3} K_2 1,62·10^{-6}	20		**E3b** **D1** **R3d**	unsicher. Wenig exper. Angaben.	S28
114	Cyclopentyl-1,1-Diessigsäure: 					
	K_1 1,60·10^{-4} K_2 1,70·10^{-7}	25	$\varkappa = 1$ $c = 0{,}005$	**E3a** **D1** **R3c**	rel. zuv. Weitere Messung: G1.	G12
115	*trans*-Cyclopentyl-1,2 Diessigsäure: 					

	K_1 3,72·10^{-5} K_2 3,72·10^{-6}	20		**E3b** **D1** **R3d**	unsicher. Wenig exper. Angaben.	S28
116	*cis*-Cyclopentyl-1,2-Diessigsäure: 					
	K_1 3,80·10^{-5} K_2 3,80·10^{-6}	20		**E3b** **D1** **R3d**	unsicher. Wenig exper. Angaben.	S28
117	3-Methylcyclopentyl-1,1-Diessigsäure: 					
	K_1 1,61·10^{-4} K_2 1,82·10^{-7}	25	$\varkappa = 1$ $c = 0{,}005$	**E3a** **D1** **R3c**	rel. zuv.	G12
118	Cyclohexan-1,1-dicarbonsäure: 					
	K_1 3,54·10^{-4} K_2 7,8·10^{-5}	25	$\varkappa = 0{,}6$ bis $0{,}8$ $\mathcal{J} = 0{,}0001$ bis $0{,}01$	**E3b** **D1** **R3b** K_1 auch **L1** **R1b**	rel. zuv.	G8
					Weitere Messung: V3.	

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
119	*trans*-Cyclohexan-1,2-dicarbonsäure: 					
	K_1 6,61·10^{-3}	18	$\varkappa = 3$	**E3a**	unsicher.	K41
	K_2 1,18·10^{-6}	19	$\mathcal{I} \geq 0{,}12$	**D1**	$\log f_\pm = A\sqrt{\mathcal{I}}$.	
120	*cis*-Cyclohexan-1,2-dicarbonsäure: 					
	pK_1 4,34 pK_2 6,77	20	$\mathcal{I} \simeq 0{,}1$	**E3a** **D1**	rel. zuv.	B39
	K_1 4,75·10^{-3}	19	$\varkappa = 3$	**E3a**	unsicher.	K41
	K_2 1,74·10^{-7}		$\mathcal{I} \geq 0{,}12$	**D1**	$\log f_\pm = A\sqrt{\mathcal{I}}$.	
121	*trans*-Cyclohexan-1,3-dicarbonsäure: 					
	K_1 4,90·10^{-5}	19	$\varkappa = 3$	**E3a**	unsicher.	K41
	K_2 1,86·10^{-6}		$\mathcal{I} \geq 0{,}12$	**D1**	$\log f_\pm = A\sqrt{\mathcal{I}}$.	

122 *cis*-Cyclohexan-1,3-dicarbonsäure:

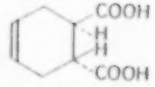


K_1 7,94·10^{-5}	16	$\varkappa = 3$	**E3a**	unsicher.	K41
K_2 3,47·10^{-6}		$\mathcal{J} \geqslant 0{,}12$	**D1**	$\log f_i = A\sqrt{\mathcal{J}}$.	

123 *trans*-Cyclohexan-1,4-dicarbonsäure:

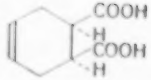
K_1 6,61·10^{-5}	16	$\varkappa = 3$	**E3a**	unsicher.	K41
K_2 3,80·10^{-6}	19	$\mathcal{J} \geqslant 0{,}12$	**D1**	$\log f_i = A\sqrt{\mathcal{J}}$.	
K_1 5,13·10^{-5}	16			Wert von (K41) neu berechnet.	W4

124 *trans*-Cyclohexen-4-1,2-dicarbonsäure:

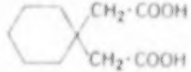
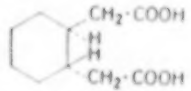
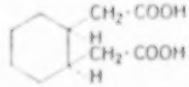


pK_1 3,95	20	$\mathcal{J} = 0{,}1$	**E3a**	rel. zuv.	B39
pK_2 5,81			**D1**		

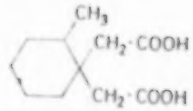
125 *cis*-Cyclohexen-4-1,2-dicarbonsäure:



pK_1 3,89	20	$\mathcal{J} = 0{,}1$	**E3a**	rel. zuv.	B39
pK_2 6,79			**D1**		

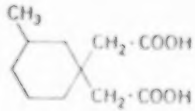
No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
126	Cyclohexyl-1,1-Diessigsäure: 					
	K_1 3,25·10⁻⁴ K_2 1,085·10⁻⁷	25	$I \geq 0{,}001$	**E1c** **R3a**	rel. zuv.	J13
	K_1 2,423·10⁻⁴ K_2 9,09·10⁻⁸	50				
	K_1 1,79·10⁻⁴ K_2 7,80·10⁻⁸	74				
	K_1 3,27·10⁻⁴ K_2 8,26·10⁻⁸	25	$\varkappa = 1$ $\varepsilon = 0{,}005$	**E3a** **D1 R3c**	rel. zuv. Weitere Messung: G1.	G12
127	*trans*-Cyclohexyl-1,2-Diessigsäure: 					
	K_1 3,17·10⁻⁴ K_2 3,80·10⁻⁶	20		**E3b** **D1 R3d**	unsicher. Wenig exper. Angaben.	S28
128	*cis*-Cyclohexyl-1,2-Diessigsäure: 					
	K_1 3,80·10⁻⁴ K_2 3,55·10⁻⁶	20		**E3b** **D1** **R3d**	unsicher. Wenig exper. Angaben.	S28

129 2-Methylcyclohexyl-1,1-Diessigsäure:



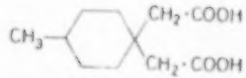
K_1 2,96·10⁻⁴ K_2 1,30·10⁻⁷	25	$\varkappa = 1$ $c = 0{,}005$	**E3a** rel. zuv. **D1 R3c**	G12

130 3-Methylcyclohexyl-1,1-Diessigsäure:



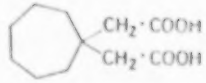
K_1 3,23·10⁻⁴ K_2 8,34·10⁻⁷	25	$\varkappa = 1$ $c = 0{,}005$	**E3a** rel. zuv. **D1 R3c**	G12

131 4-Methylcyclohexyl-1,1-Diessigsäure:

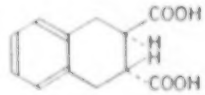


K_1 3,23·10⁻⁴ K_2 8,02·10⁻⁷	25	$\varkappa = 1$ $c = 0{,}005$	**E3a** rel. zuv. **D1 R3c**	G12

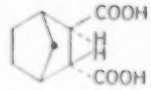
132 Cycloheptyl-1,1-Diessigsäure:



Nur K_c Werte. G1

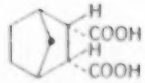
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
133	Perhydrodiphensäure:					
	(*a*) K_1 1,10·10^{-4} K_2 2·10^{-7} (*b*) K_1 1,42·10^{-5} K_2 1,1·10^{-8}	20		**E3b** (*a*): F_p = 220°C **D1 R3d** (*b*): F_p = 224°C	schlecht löslich. unsicher.	S28
134	*trans*-Tetrahydronaphthalin-2,3-dicarbonsäure: 					
	K_1 1,0·10^{-3} K_2 2,0·10^{-6}	20		**E3b** **D1 R3d**	unsicher.	S28
135	*cis*-Tetrahydronaphthalin-2,3-dicarbonsäure:					
	K_1 1,05·10^{-3} K_2 3,39·10^{-7}	20		**E3b** **D1 R3d**	rel. zuv.	S28

136 *trans*-Hexahydro-3,6-Endomethylen-*o*-Phthalsäure:



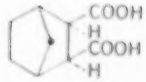
pK_1 4,07 pK_2 5,66	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	rel. zuv.	B39

137 *a-cis*-Hexahydro-3,6-Endomethylen-*o*-Phthalsäure:



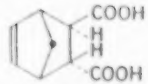
pK_1 4,09 pK_2 7,38	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	rel. zuv.	B39

138 *β-cis*-Hexahydro-3,6-Endomethylen-*o*-Phthalsäure:

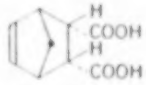
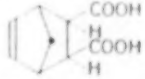
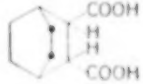
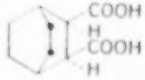


pK_1 4,52 pK_2 6,72	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	rel. zuv.	B39

139 *trans*-Δ^4-Tetrahydro-3,6-Endomethylen-*o*-Phthalsäure:



pK_1 4,06 pK_2 5,74	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	rel. zuv.	B39

No.	*Name, Formel u. Dissoziationskonstante k*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
140	*a-cis*-Δ^3-Tetrahydro-3,6-Endomethylen-*o*-Phthalsäure: 					
	pk_1 4,25 pk_2 7,04	20	$J = 0,1$	**E3a** **D1**	rel. zuv.	B39
141	*β-cis*-Δ^3-Tetrahydro-3,6-Endomethylen-*o*-Phthalsäure: 					
	pk_1 4,46 pk_2 6,63	20	$J = 0,1$	**E3a** **D1**	rel. zuv.	B39
142	*trans*-Hexahydro-3,6-Endoäthylen-*o*-Phthalsäure: 					
	pk_1 4,09 pk_2 6,15	20	$J = 0,1$	**E3a** **D1**	rel. zuv.	B39
143	*cis*-Hexahydro-3,6-Endoäthylen-*o*-Phthalsäure: 					

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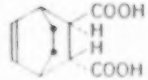
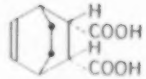
	pK_1 4,79 pK_2 6,95	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	rel. zuv.	B39

144 *trans*-Δ^4-Tetrahydro-3,6-Endoäthylen-*o*-Phthalsäure:



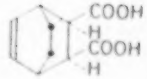
	pK_1 4,15 pK_2 7,82	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	rel. zuv.	B39

145 *α-cis*-Δ^4-Tetrahydro-3,6-Endoäthylen-*o*-Phthalsäure:



	pK_1 4,66 pK_2 6,77	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	rel. zuv.	B39

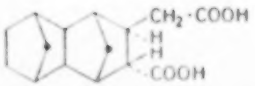
146 *β-cis*-Δ^4-Tetrahydro-3,6-Endoäthylen-*o*-Phthalsäure:



	pK_1 4,56 pK_2 6,87	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	rel. zuv.	B39

147 *trans*-$C_{14}H_{18}O_4$-dicarbonsäure:

	pK_1 4,52 pK_2 6,16	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	unsicher.	B39

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
148	*o-cis*-$C_{14}H_{18}O_4$-dicarbonsäure:					
	pK_1 4,15 pK_2 7,82	20	$I = 0,1$	**E3a** **D1**	unsicher.	B39
149	*β-cis*-$C_{14}H_{18}O_4$-dicarbonsäure:					
	pK_1 4,72 pK_2 6,87	20	$I = 0,1$	**E3a** **D1**	unsicher.	B39
150	*o-trans*-$C_{15}H_{20}O_4$-dicarbonsäure:					
	pK_1 4,25 pK_2 6,06	20	$I = 0,1$	**E3a** **D1**	unsicher.	B39
151	*β-trans*-$C_{15}H_{20}O_4$-dicarbonsäure: 					

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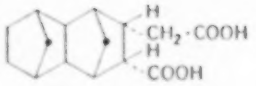
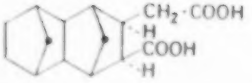
	pK_1 4,46 pK_2 6,09	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	unsicher.	B39

152 *α-cis*-$C_{15}H_{20}O_4$-dicarbonsäure:



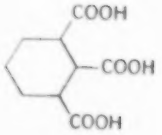
	pK_1 4,69 pK_2 6,22	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	unsicher.	B39

153 *β-cis*-$C_{15}H_{20}O_4$-dicarbonsäure:



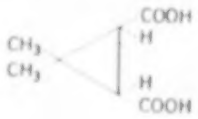
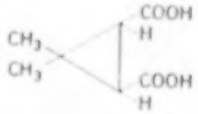
	pK_1 4,45 pK_2 5,63	20	$\mathcal{J} = 0{,}1$	**E3a** **D1**	unsicher.	B39

154 1,2,3-Cyclohexan-tricarbonsäure:



	K_1 $13{,}3 \cdot 10^{-5}$ K_2 $14{,}0 \cdot 10^{-5}$ K_3 $14{,}8 \cdot 10^{-9}$	23		unsicher. Nähere Angaben fehlen.	B10

Dazu noch verschiedene Ester dieser Säure.

No.	*Name, Formel u. Dissoziationskonstante k*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
155	*trans*-Caronsäure: 					
	k_1 1,52·10^{-1} k_2 4,78·10^{-6}	25	$I \geq 0{,}001$	**E1c** **R3a**	rel. zuv.	J13
	k_1 1,21·10^{-1} k_2 3,58·10^{-6}	50				
	k_1 1,03·10^{-1} k_2 2,64·10^{-6}	74				
	k_1 2,52·10^{-1} k_2 5,60·10^{-6}	27	I = 0,001 bis 0,009	**E3b** **D1**	unsicher.	A4
156	*cis*-Caronsäure: 					
	k_1 4,59·10^{-3} k_2 4,94·10^{-9}	25	$I \geq 0{,}001$	**E1c** **R3a**	rel. zuv.	J13
	k_1 3,80·10^{-3} k_2 4,46·10^{-9}	50				
	k_1 2,83·10^{-3} k_2 3,81·10^{-9}	74				

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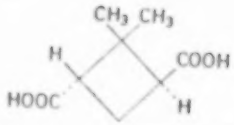
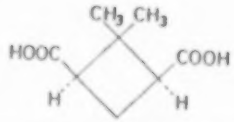
	K_1 2,42·10⁻⁴ K_2 4,76·10⁻⁹	26,8	$\mathcal{I}$ = 0,0008 bis 0,006	**E3b** **D1**	unsicher.	A4
157	*trans*-Norpinsäure: 					
	K_1 2,66·10⁻⁴ K_2 5,73·10⁻⁶	21,8	$\mathcal{I}$ = 0,001 bis 0,008	**E3b** **D1**	unsicher.	A4
158	*cis*-Norpinsäure: 					
	K_1 1,47·10⁻⁴ K_2 2,84·10⁻⁶	21,8	$\mathcal{I}$ = 0,001 bis 0,008	**E3b** **D1**	unsicher.	A4

12I

159	Monofluor-Essigsäure: $CH_2F{\cdot}COOH$					
	(*c*) 2,789·10⁻³ 2,684 2,596 2,490 2,379	15 20 25 30 35	$\varkappa$ = 0,1 $\mathcal{I}$ = 0,0003 bis 0,0015	**L2** ähnl. **R1c**	sehr zuv.	I6
	K_c 2,18·10⁻³	25		**L2**	unsicher. Keine exper. Angaben. Sonst wie bei Trifluor-Essigsäure (H31).	H33

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
160	Monochlor-Essigsäure: $CH_2ClCOOH$					
	(c) 1,51·10⁻³ (1) 1,48·10⁻³ (2)	25	$\mathcal{I}$ = 0,01 bis 4	**Kat.**	unsicher. Wert (1) aus Messungen an Aceton-Jod-Reaktion, (2) an Äthylacetatverseifung. In Gegenwart von NaCl, wegen zweimaliger Extrapolation auf $c_{NaCl}=0$ bzw. $c_{Säure}=0$ als Näherung für thermodynamische Konstante anzusehen. Autokatalytischer Effekt und katalytische Wirkung des Anions vernachlässigt.	D4
	(c) 1,49·10⁻³	18	$\varkappa$ = 2 (?) $\mathcal{I}$ = 0,01 bis 3	**E2b**	rel. zuv. Hydrolyse (vgl. L6).	L11
	(m) 1,528·10⁻³ 1,491 1,437 1,378 1,310 1,229	0 10 18 25 32 40	$\varkappa$ = 1 $\mathcal{I}$ = 0,02 bis 0,2	**E1a**	rel. zuv. E.M.K.-Werte nicht genau reproduzierbar, ebenso verwendete Daten von Harned u. Wright oberhalb 30 C (H23). Vgl. dazu Briegleb u. Bieber (B49) (a.a. Kortschak (K35)).	W11
	(c) 1,398·10⁻³	0	$\varkappa$ = 1 $\mathcal{I}$ = 0,001 bis 0,004	**L1** **R1b** **K2a**	rel. zuv. Glaszellen. Unsichere Solvenskorr. Hydrolyse (vgl. I6).	S6
	(c) 1,39·10⁻³	25	c = 0,001 bis 0,06	**L2**	unsicher. In experimenteller Originalarbeit (O5) keine Angaben über $\varkappa$ und Korrekturen. K aus K_c mit f von HCl berechnet. Meßdaten unsicher.	R3
	(c) 1,397·10⁻³	25	$\mathcal{I}$ = 0,0001 bis 0,03	**L1**	rel. zuv. Original der experimentellen Arbeit war nicht zugänglich (S16). Hydrolyse (vgl. I6).	M6

	(*c*) 1,337·10⁻³	25	$\mathcal{J}$ = 0,003 bis 0,03	**O2**	rel. zuv. Relative Konstante gegen 2,6-Dinitro-Phenol gemessen. *K* für letzteres nicht direkt gemessen, sondern aus dem Konstantenverhältnis zweier anderer Säuren ermittelt. Keine Korrektur für Reaktion der Puffermischung mit H_3O und der zugesetzten Indikatorsäure.	M21
	(*c*) 1,430·10⁻³ 1,394 1,359 1,3079 1,2594	15 20 25 30 35	$\varkappa$ = 0,1 $\mathcal{J}$ = 0,0003 bis 0,001	**L2** ähnl. **R1c**	sehr. zuv.	I6
	(*c*) 1,413·10⁻³	20	$\mathcal{J}$ = 0,0015 bis 0,02	**Kat.**	rel. zuv. Messung der Hydrolysegeschwindigkeit von Dimethyl-Acetal. Es wurde nachgewiesen, daß keine Säurekatalyse vorliegt und die Konstante für spontane Reaktion $< 10^{-8}$ (B7).	G22
					Weitere Messungen: B33; D3; H18; L1.	
161	Monobrom-Essigsäure: $CH_2Br{\cdot}COOH$					
	(*c*) 1,3331·10⁻³ 1,2963 1,2530 1,2078 1,1588	15 20 25 30 35	$\varkappa$ = 0,1 $\mathcal{J}$ = 0,0003 bis 0,001	**L2** ähnl. **R1c**	sehr zuv.	I6
	(*c*) 1,29·10⁻³	18	$\varkappa$ = 0,3 $\mathcal{J}$ = 0,01 bis 3	**E2b**	zuv.	I.9
162	Monojod-Essigsäure: $CH_2J{\cdot}COOH$					
	(*c*) 7,190·10⁻⁴ 6,946 6,680 6,406 6,126	15 20 25 30 35	$\varkappa$ = 0,1 $\mathcal{J}$ = 0,0001 bis 0,001	**L2** ähnl. **R1c**	sehr. zuv.	I6
	(*c*) 7,0·10⁻⁴	18	$\varkappa$ = 0,3 $\mathcal{J}$ = 0,01 bis 3	**E2b**	zuv.	I.9

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
163	Cyan-Essigsäure: $NC{\cdot}CH_2{\cdot}COOH$					
	(c) $3{,}55{\cdot}10^{-3}$	25	$\varkappa = 1$ $\mathcal{J} = 0{,}0005$ bis $0{,}06$	**L1** **R1b**	rel. zuv. (s.u.). Wie bei Ameisensäure (D1).	D1
	(c) $3{,}50{\cdot}10^{-3}$	25	$\varkappa = 1$ $c = 0{,}0005$ bis $0{,}06$	**L1** **R1b**	rel. zuv. (s.u.). Meßdaten bei kleinsten Konzentrationen unsicher.	M3
	(c) $3{,}360{\cdot}10^{-3}$	25	$\mathcal{J} = 0{,}00001$ bis $0{,}006$	**L1** **R1b** **K1a**	zuv. (s.u.). Keine Angaben, wie überschüssige Säure berücksichtigt wurde.	S5
	(c) $3{,}42{\cdot}10^{-3}$	25	$\varkappa = 0{,}15$ bis $0{,}3$ $c = 0{,}0001$ bis $0{,}001$	**L2** ähnl. **R1a** ähnl. **R1c** **K1d**	zuv. Einfluß vorhandener apparativer Mängel (Erdung, Zellform läßt Parkereffekt erwarten, Wasserthermostat) wegen Größe der Konstanten wahrscheinlich gering (vgl. dazu B21 u. 14).	I5
	(c) $2{,}618{\cdot}10^{-3}$	25	$\mathcal{J} = 0{,}003$ bis $0{,}03$	**O2**	rel. zuv. Relative Konstante gegen *m*-Kresolpurpur gemessen. *K* für letzteres aus Messungen mit HCl. Keine Korr. für Reaktion der Puffermischung mit H_2O u. mit der Indikatorsäure. (Differenz gegen andere zuverlässige Werte kann nicht geklärt werden.)	M21
					Weitere Messung: B15.	
164	Dichlor-Essigsäure: $CHCl_2{\cdot}COOH$					
	(c) $4{,}3{\cdot}10^{-2}$	25	$c = 0{,}13$ bis $0{,}53$	**Kat.**	unsicher. Aus Messungen der Wasseranlagerung an iso-Buten. Katalytische Wirkung der freien Säure u. des Anions vernachlässigt. Für $f_\pm$ wurden Werte von Essigsäure bei gleichem $\mathcal{J}$ verwendet.	C16

	(*c*) $5{,}0 \cdot 10^{-2}$	25	$c = 0{,}05$	**Kat.**	unsicher. Aus Messung der Verseifungsgeschwindigkeit von Äthylacetat. Autokatalytischer Effekt u. Wirkung des Anions vernachlässigt.	D4
	(*c*) $3{,}32 \cdot 10^{-2}$	25	$\mathcal{J} = 0{,}08$	**Kat.**	unsicher. Aus Messungen der Verseifungsgeschwindigkeit von Äthylacetat. Katalytische Wirkung der undissoziierten Säure vernachlässigt. Für f_1 wurden Werte von Wasser verwendet.	H18
	(*c*) $5{,}53 \cdot 10^{-2}$ 5,83	25 18	$\varkappa = 0{,}9$ $\mathcal{J} = 0{,}001$ bis 0,2	**L1** ähnl. **RIb**	rel. zuv. Für f_1 wurden Werte von HCl bei gleichem $\mathcal{J}$ verwendet (nicht publiziert).	R3
165	Trifluor-Essigsäure: $CF_3 \cdot COOH$					
	K_c 0,588 0,533	25 35	$\varkappa = 5$ (?) $\mathcal{J} = 0{,}001$ bis 0,09	**L2** u. **E3b** **D1**	unsicher. Sehr wenig experimentelle Angaben. K_c berechnet mit Dissoziationsgrad $\alpha = \Lambda_c/\Lambda_0$. Λ_0 durch Extrapolation der gemessenen Λ_c. Keine Solvenskorr. Tauchelektroden.	H31
					Weitere Messungen: S34.	
166	Trichlor-Essigsäure: $CCl_3 \cdot COOH$					
	(*c*) 0,217 0,232	20 25	$\mathcal{J} = 0{,}003$ bis 0,01	**O4**	zuv. Kolorimetrisch mit α-Dinitro-Phenol als Indikator.	H4
	(*c*) 1	25	$\mathcal{J} = 0{,}16$ bis 0,6	**Kat.**	unsicher. Wie bei Dichlor-Essigsäure (C16).	C16
					Weitere Messungen: B33; S12.	
167	α-Chlor-Propionsäure: $CH_3 \cdot CHCl \cdot COOH$					
	(*c*) $1{,}32 \cdot 10^{-3}$	18	$\varkappa = 0{,}3$ (?) $\mathcal{J} = 0{,}01$ bis 3	**E2b**	zuv.	L9

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
168	β-Chlor-Propionsäure: $CH_2Cl{\cdot}CH_2{\cdot}COOH$					
	K_c 1,01·10 $^{-3}$	25	ϵ = 0,01 bis 0,5	**Kat.**	unsicher. Aceton-Jod-Reaktion.	D3
	(c) 8,0·10 $^{-5}$	18	$\varkappa$ = 0,3 (?) $\bar{J}$ = 0,005 bis 3	**E2b**	zuv.	L9
169	α-Brom-Propionsäure: $CH_3{\cdot}CHBr{\cdot}COOH$					
	(c) 1,07·10 $^{-3}$	18	$\varkappa$ = 0,3 (?) $\bar{J}$ = 0,01 bis 3	**E2b**	zuv.	L9
170	β-Brom-Propionsäure: $CH_2Br{\cdot}CH_2{\cdot}COOH$					
	(c) 1,02·10 $^{-4}$	18	$\varkappa$ = 0,3 (?) $\bar{J}$ = 0,005 bis 3	**E2b**	zuv.	L9
171	α-Jod-Propionsäure: $CH_3{\cdot}CHJ{\cdot}COOH$					
	(c) 7,8·10 $^{-4}$	18	$\varkappa$ = 0,3 (?) $\bar{J}$ = 0,01 bis 3	**E2b**	zuv.	L9
172	β-Jod-Propionsäure: $CH_2J{\cdot}CH_2{\cdot}COOH$					
	(c) 8,2·10 $^{-5}$	18	$\varkappa$ = 0,3 (?) $\bar{J}$ = 0,01 bis 3	**E2b**	zuv.	L9
173	α-Cyan-Propionsäure: $CH_3{\cdot}CH(CN){\cdot}COOH$					
	K_c 4,27·10 $^{-3}$	?	ϵ = 0,001 bis 0,1	**L2**	unsicher. K_c-Wert nach Ostwald'schem Verdünnungsgesetz berechnet. Säure wurde von H_2O zersetzt unter Bildung von Blausäure.	W7

174 β-Cyan-Propionsäure: $NC{\cdot}(CH_2)_2{\cdot}COOH$

(c)	$1{,}02{\cdot}10^{-4}$	25	$\varkappa = 0{,}15$ bis $0{,}3$ $\mathcal{J} = 0{,}0001$ bis $0{,}001$	**L1** ähnl. **R1a** ähnl. **R1c** **K1d**	rel. zuv. Apparative Mängel (Erdung, Zellform läßt Parkereffekt erwarten, Wasserthermostat). Es wurde keine Hydrolyse der CN-Gruppe beobachtet. (vgl. dazu W7).	15
					Weitere Messungen: W7.	

175 β,β,β-Trifluor-Propionsäure: $CF_3{\cdot}CH_2{\cdot}COOH$

K_c	$9{,}52{\cdot}10^{-4}$	35	$\varkappa = 5$ (?)	**L1**	unsicher.	H31
	8,65	25	$\mathcal{J} = 0{,}0004$ bis $0{,}04$	**R1b**	Sehr wenig experimentelle Angaben; keine Solvenskorr. Tauchelektroden.	

176 α-Chlor-iso-Buttersäure: $(CH_3)_2CCl{\cdot}COOH$

(c)	$1{,}06{\cdot}10^{-3}$	18	$\varkappa = 0{,}3$ (?) $\mathcal{J} = 0{,}01$ bis 3	**E2b**	zuv.	L9

177 γ-Cyan-n-Buttersäure: $NC{\cdot}(CH_2)_3{\cdot}COOH$

(c)	$3{,}66{\cdot}10^{-5}$	25	$\varkappa = 0{,}15$ bis $0{,}3$ $\mathcal{J} = 0{,}0001$ bis $0{,}001$	**L1** ähnl. **R1a** ähnl. **R1c** **K1d**	rel. zuv. Apparative Mängel (Erdung, Zellform läßt Parkereffekt erwarten; Wasserthermostat).	15

178 α-Cyan-iso-Buttersäure: $(CH_3)_2C(CN){\cdot}COOH$

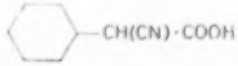
(c)	$3{,}80{\cdot}10^{-3}$	25	$\varkappa = 0{,}15$ bis $0{,}3$ $\mathcal{J} = 0{,}0001$ bis $0{,}001$	**L1** ähnl. **R1a** ähnl. **R1c** **K1d**	rel. zuv. Wie bei γ-Cyan-n-Buttersäure (15).	15

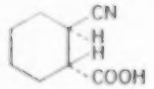
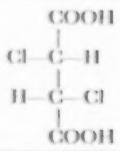
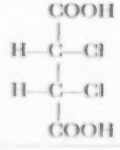
179 γ,γ,γ-Trifluor-n-Buttersäure: $CF_3{\cdot}(CH_2)_2{\cdot}COOH$

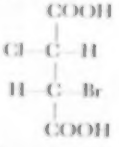
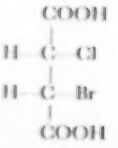
K_c	$6{,}98{\cdot}10^{-5}$	25	$\mathcal{J} = 0{,}0004$ bis $0{,}04$	**L1**	unsicher.	H31
	6,80	35		**R1b**	Wie bei Trifluor-Propionsäure (H31).	
K_c	$7{,}0{\cdot}10^{-5}$	25		**E3b**	unsicher. Sehr wenig experimentelle Angaben. Aus pH bei halber Neutralisation nach $pH = pK$ berechnet.	M1

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
180	Heptafluor-n-Buttersäure: $CF_3{\cdot}(CF_2)_2{\cdot}COOH$					
	K_c 0,678	25	$\mathcal{J} = 0{,}001$ bis 0,09	**L1**	unsicher.	H31
	0,625	35			Wie bei Trifluor-Essigsäure (H31).	
181	α-Äthyl-β-Brom-Propionsäure: $CH_3{\cdot}CH_2{\cdot}CH(CH_2Br){\cdot}COOH$					
	(c) $1{,}2{\cdot}10^{-4}$	18	$\varkappa = 0{,}3$ (?)	**E2b**	unsicher.	L9
			$\mathcal{J} = 0{,}01$ bis 3		Die schnelle Hydrolyse in den KCl-Lösungen wurde durch Aufnahme der E.M.K. der Kette als Funktion der Zeit und Extrapolation auf den Zeitpunkt der Herstellung der Lösung berücksichtigt.	
182	δ,δ,δ-Trifluor-n-Valeriansäure: $CF_3{\cdot}(CH_2)_3{\cdot}COOH$					
	K_c $3{,}2{\cdot}10^{-5}$	?		**E3b**	unsicher.	H32
					Keine experimentellen Angaben.	
183	δH-Octafluor-n-Valeriansäure: $CHF_2{\cdot}(CF_2)_3{\cdot}COOH$					
	K_m $2{,}23{\cdot}10^{-3}$	?		**E3b**	unsicher.	A10
					Keine Angaben.	
184	γ,γ,δ,δ,ε,ε,ε-Heptafluor-n-Capronsäure: $CF_3{\cdot}(CF_2)_2{\cdot}(CH_2)_2{\cdot}COOH$					
	K_c $6{,}6{\cdot}10^{-5}$	25		**E3b**	unsicher.	M1
					Wie bei Trifluor-n-Buttersäure (M1).	
185	Hochfluorierte Önanthsäure: $CHF_2{\cdot}(CF_2)_5{\cdot}COOH$					
	K_m $2{,}08{\cdot}10^{-3}$	?		**E3b**	unsicher.	A10
					Keine Angaben.	
186	Hochfluorierte Pelargonsäure: $CHF_2{\cdot}(CF_2)_7{\cdot}COOH$					
	K_m $2{,}51{\cdot}10^{-3}$	?		**E3b**	unsicher.	A10
					Keine Angaben.	

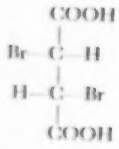
187	α-Fluor-Acrylsäure: $CH_2{:}CF{\cdot}COOH$					
	(c) $2{,}79{\cdot}10^{-3}$	25		**L2**	unsicher. Wie bei Fluor-Essigsäure (H33).	H33
188	β,β-Difluor-Acrylsäure: $CF_2{:}CH{\cdot}COOH$					
	K_c $6{,}8{\cdot}10^{-4}$	25		**L2**	unsicher. Wie bei Fluor-Essigsäure (H33).	H33
189	Trifluor-Acrylsäure: $CF_2{:}CF{\cdot}COOH$					
	(c) $1{,}61{\cdot}10^{-2}$	25		**L2**	unsicher. Wie bei Fluor-Essigsäure (H33).	H33
190	*trans*-β-Chlor-Acrylsäure: $ClCH{=}HC{\cdot}COOH$					
	K_c $2{,}22{\cdot}10^{-4}$	18	$\epsilon = 0{,}1$	**E3b** **R3b**	unsicher. Wie bei *cis*-β-Chlor-Acrylsäure (B2).	B2
191	*cis*-β-Chlor-Acrylsäure: $HCCl{=}HC{\cdot}COOH$					
	K_c $4{,}77{\cdot}10^{-4}$	18	$\epsilon = 0{,}1$	**E3b** **R3b**	unsicher. Original der exp. Arbeit nicht zugänglich (B30). Unsichere Rechenmethode. Diffusionspotentiale.	B2
192	Trichlor-Acrylsäure: $CCl_2{:}CCl{\cdot}COOH$					
	K_c $7{,}0{\cdot}10^{-2}$	25		**L2**	unsicher. Wie bei Fluor-Essigsäure (H33).	H33
	K_c $7{,}0{\cdot}10^{-2}$ 6,5	25	$\epsilon = 0{,}002$ bis $0{,}03$	**L1**	unsicher. Dissoziationsgrad berechnet nach $\alpha = \Lambda_c/\Lambda_\infty$. Wenig exp. Angaben.	B43
193	α-Chlor-Crotonsäure: $CH_3{\cdot}CH{:}CCl{\cdot}COOH$					
	(c) $6{,}00{\cdot}10^{-4}$	25	$\varkappa = 2$ $\epsilon = 0{,}04$ bis $0{,}001$	**L1**	unsicher. Diss. Grad berechnet nach $\alpha = \Lambda_v/\Lambda_0$. Λ_0 nach Regel von Ostwald erhalten.	K24
					Weitere Messungen: R2.	

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
194	α-Chlor-Vinyl-Essigsäure: CH_2:CH·CHCl·COOH					
	(c) $2{,}9 \cdot 10^{-3}$	25	$\varkappa = 2$ $c = 0{,}002$ bis $0{,}06$	**L2**	unsicher. Wie bei α-Chlor-Crotonsäure (K24).	K24
					Weitere Messungen: R2.	
195	γ,γ,γ-Trifluor-Crotonsäure: CF_3·CH:CH·COOH					
	K_c $4{,}5 \cdot 10^{-4}$	25		**L2**	unsicher. Wie bei Fluor-Essigsäure (H33).	H33
	K_c $3{,}3 \cdot 10^{-4}$	25		**E3b**	unsicher. Wie bei Trifluor-n-Buttersäure (M1).	M1
	K_c $7{,}1 \cdot 10^{-4}$				unsicher. Keine experimentellen Angaben.	W3
	K_c $7{,}9 \cdot 10^{-4}$	25	$I = 0{,}001$ bis $0{,}0005$	**L1** **E3a**	unsicher. Sehr wenig exper. Angaben. K-Werte aus pH-Messungen nach pH = pK bei halber Neutralisation berechnet.	H27
196	Heptafluor-n-propyl-Acrylsäure: $CF_3(CF_2)_2$·CH:CH·COOH					
	K_c $5{,}9 \cdot 10^{-4}$	25		**E3b**	unsicher. Wie bei Trifluor-n-Buttersäure (M1).	M1
197	Cyclohexyl-Cyan-Essigsäure: 					
	(c) $4{,}30 \cdot 10^{-3}$	25	$\varkappa = 0{,}15$ bis $0{,}3$ $c = 0{,}0001$ bis $0{,}001$	**L2** ähnl. **R1a** ähnl. **R1c** **K1d**	rel. zuv. Wie bei γ-Cyan-n-Buttersäure (I5).	I5

198	*trans*-1-Cyan-Cyclohexan-2-carbonsäure: 					
	(*c*) 1,365·10^{-4}	25	$\varkappa = 0{,}15$ bis 0,3 $c = 0{,}0001$ bis 0,001	**L2** ähnl. **R1a** ähnl. **R1c** **K1d**	rel. zuv. Wie bei γ-Cyan-n-Buttersäure (15).	15
199	Monobrom-Bernsteinsäure: COOH·CHBr·CH_2·COOH					
	K_1 2,05·10^{-3} K_2 2,04·10^{-5}	19 50	$\mathcal{J} = 0{,}05$	K_1 nach **E3a** u. **D1** K_2 **Kat.**	unsicher. Zersetzung unter HBr-Abspaltung.	O1
200	*rac.*-α,α'-Dichlor-Bernsteinsäure: 					
	K_1 3,72·10^{-2} K_2 1,80·10^{-3}	16	$\mathcal{J} \geq 0{,}1$	**E3a** **D1**	unsicher. $\log f_i = A\sqrt{\mathcal{J}}$.	K37
	K_1 3,47·10^{-2} K_2 1,38·10^{-3}	20	$\mathcal{J} = 0{,}1$	**E3b** **D1** **R3c**	unsicher.	B39
	K_1 3,72·10^{-2} K_2 1,55·10^{-3}	20		u. **E3a** **D1** **R3c**		
201	*meso*-α,α'-Dichlor-Bernsteinsäure: 					

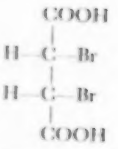
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	K_1 3,61·10 $^{-2}$	20	$\mathcal{J} \geq 0{,}1$	**E3a**	unsicher.	K37
	K_2 9,40·10 $^{-4}$	18		**D1**	$\log f_\pm = A\sqrt{\mathcal{J}}$.	
	K_1 3,02·10 $^{-2}$	20	$\mathcal{J} = 0{,}1$	**E3a**	unsicher.	B39
	K_2 1,15·10 $^{-3}$			**D1**		
				R3c		
	K_1 3,24·10 $^{-2}$	20		u. **E3b**		
	K_2 1,08·10 $^{-3}$			**D1**		
				R3c		
202	*threo*-α-Chlor-α′-Brom-Bernsteinsäure:					
						
	K_1 3,5·10 $^{-2}$	20	$\mathcal{J} \geq 0{,}1$	**E3a**	unsicher.	K37
	K_2 1,7·10 $^{-3}$			**D1**	$\log f_\pm = A\sqrt{\mathcal{J}}$.	
203	*erythro*-α-Chlor-α′-Brom-Bernsteinsäure:					
						
	K_1 3,7·10 $^{-2}$	19	$\mathcal{J} \geq 0{,}1$	**E3a**	unsicher.	K37
	K_2 2,5·10 $^{-3}$			**D1**	$\log f_\pm = A\sqrt{\mathcal{J}}$.	

204 *rac.*-α,α'-Dibrom-Bernsteinsäure:



K_1 3,72·10^{-2}	20	$\mathcal{J} = 0{,}1$	**E3a** **D1** **R3c** **E3b** **D1** **R3c**	unsicher.	B39
K_1 3,80·10^{-2} K_2 5,76·10^{-4}	20				
K_1 4,15·10^{-2} K_2 8,17·10^{-4}	18	$\mathcal{J} \geq 0{,}1$	**E3a** **D1**	unsicher. $\log f_i = A\sqrt{\mathcal{J}}$.	K37

205 *meso*-α,α'-Dibrom-Bernsteinsäure:



K_1 2,76·10^{-2}	20	$\mathcal{J} = 0{,}1$	**E3a** **D1** **R3c** **E3b** **D1** **R3c**	unsicher.	B39
K_1 3,09·10^{-2} K_2 1,95·10^{-3}	20				
K_1 3,57·10^{-2} K_2 2,39·10^{-3}	17 19	$\mathcal{J} \geq 0{,}1$	**E3a** **D1**	unsicher. $\log f_i = A\sqrt{\mathcal{J}}$.	K37

Bezeichnung 122–122

No.	Name, Formel u. Dissoziationskonstante K	I	t (°C)	Bemerkungen	Methode	Kritik	Lit.
206	Glykolsäure: $HO{\cdot}CH_2{\cdot}COOH$						
	(*m*) $1{,}334\cdot10^{-4}$	0,3		$J = 0{,}005$ bis $0{,}08$	**E1a**	sehr zuv.	N7
	1,332	12,5					
	1,476	25,0					
	1,469	37,5					
	1,416	50,0					
	$1{,}46\cdot10^{-4}$	18		$J = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	L11
	$1{,}45\cdot10^{-4}$ (1)	25		$J = 0{,}05$	**E2c**	zuv.	K7
	$1{,}51\cdot10^{-4}$ (2)					(1) Bezugssäure: Essigsäure.	
						(2) Bezugssäure: Benzoesäure.	
	$1{,}53\cdot10^{-4}$	18		$J = 0{,}002$ bis $0{,}003$	**E2b** **D3**	rel. zuv.	A6
	$1{,}393\cdot10^{-4}$	25		$J = 0{,}003$ bis $0{,}07$	**O2**	rel. zuv.	M21
						Weitere Messungen: D3; D4; P4; V1.	
207	Äthoxy-Essigsäure: $CH_3CH_2O{\cdot}CH_2{\cdot}COOH$						
	$2{,}23\cdot10^{-3}$	18		$J = 0{,}1$ bis $0{,}03$	**E2b**	zuv.	L10
208	Cyclopentyloxy-Essigsäure:						
	$2{,}00\cdot10^{-3}$	25			**L**	unsicher. Ohne nähere Angaben.	M28

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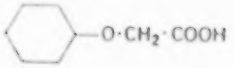
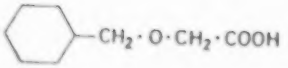
209 Cyclohexyl-oxy-Essigsäure:



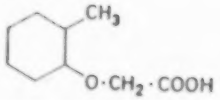
$2{,}90 \cdot 10^{-4}$	25	L	unsicher. Ohne nähere Angaben.	M28

210 Cyclohexylmethoxy-Essigsäure:



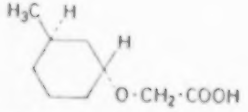
$1{,}25 \cdot 10^{-4}$	25	L	unsicher. Ohne nähere Angaben.	M28

211 2-Methylcyclohexyl-oxy-Essigsäure:

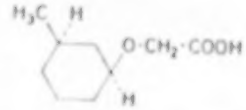
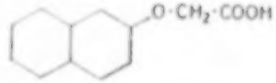
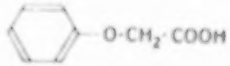
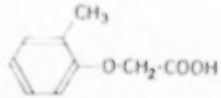


$1{,}60 \cdot 10^{-4}$	25	L	unsicher. Ohne nähere Angaben.	M28

212 *trans*-3-Methylcyclohexyl-oxy-Essigsäure:



$1{,}55 \cdot 10^{-4}$	25	L	unsicher. Ohne nähere Angaben.	M28

No.	*Name, Formel u. Dissoziations-konstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
213	*cis*-3-Methylcyclohexyl-oxy-Essigsäure: 					
	$1{,}40 \cdot 10^{-3}$	25		**L**	unsicher. Ohne nähere Angaben.	M28
214	Dekahydronaphthyl-oxy-Essigsäure: 					
	$2{,}30 \cdot 10^{-3}$	25		**L**	unsicher. Ohne nähere Angaben.	M29
215	Phenoxy-Essigsäure: 					
	$6{,}75 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	rel. zuv.	H29
	$7{,}5 \cdot 10^{-4}$	18	$\bar{f} = 0{,}005$ bis $0{,}03$	**E2b**	rel. zuv.	L10
216	o-Methylphenoxy-Essigsäure: 					
	$5{,}93 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	rel. zuv.	H23

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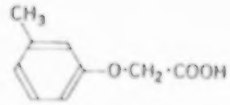
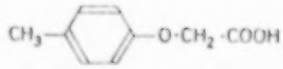
217 *m*-Methylphenoxy-Essigsäure:



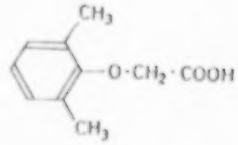
$6{,}27 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	rel. zuv.	H23

218 *p*-Methylphenoxy-Essigsäure:



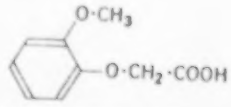
$6{,}09 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	rel. zuv.	H23

219 2,6-Dimethylphenoxy-Essigsäure:

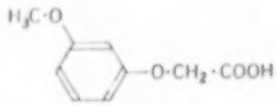
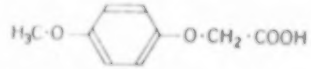


$4{,}41 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	rel. zuv.	H23

220 *o*-Methoxyphenoxy-Essigsäure:

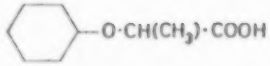


$5{,}88 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	rel. zuv.	H23

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
221	*m*-Methoxyphenoxy-Essigsäure: 					
	$7{,}22 \cdot 10^{-4}$	25	c = 0,008 bis 0,1	**E1a**	rel. zuv.	H23
222	*p*-Methoxyphenoxy-Essigsäure: 					
	$6{,}13 \cdot 10^{-4}$	25	c = 0,008 bis 0,1	**E1a**	rel. zuv.	H23
	Substituierte Phenoxy-Essigsäuren siehe **125**.					
223	Milchsäure: $CH_3 \cdot CH(OH) \cdot COOH$					
	(*c*) $1{,}317 \cdot 10^{-4}$	0	$\varkappa$ = 0,4	**L1**	sehr zuv.	M10
	1,339	5	I = 0,00006 bis 0,03	**K1a**		
	1,356	10		**R1b**		
	1,375	15				
	1,389	20				
	1,389	22				
	1,389	23				
	1,389	24				
	1,387	25				
	1,378	30				
	1,359	35				
	1,348	38				
	1,339	40				
	1,303	45				
	1,274	50				

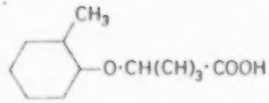
	(*m*) $1{,}288 \cdot 10^{-4}$	0,3	$\mathcal{J} = 0{,}006$ bis 0,06	**E1a**	zuv.	N9
	1,361	12,5				
	1,374	25,0				
	1,337	37,5				
	1,271	50,0				
	$1{,}38 \cdot 10^{-4}$	18	$\mathcal{J} = 0{,}02$ bis 0,03	**E2b**	zuv.	L11
					Weitere Messungen: A14; B31.	

224 α-(Cyclohexyl-oxy)-Propionsäure:



$2{,}30 \cdot 10^{-4}$	25		**L**	unsicher. Nähere Angaben fehlen.	M29

225 α-(2-Methylcyclohexyl-oxy)-Propionsäure:



$2{,}25 \cdot 10^{-4}$	25		**L**	unsicher. Nähere Angaben fehlen.	M29

226 Dimethyl-Glykolsäure: $CH_3 \cdot C(CH_3)(OH) \cdot COOH$

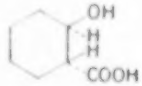
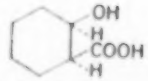
$9{,}2 \cdot 10^{-5}$	18	$\mathcal{J} = 0{,}01$ bis 0,03	**E2b**	rel. zuv. Weitere Messungen: K_c'-Werte V1.	L10

227 Methyl-Äthyl-Glykolsäure: $CH_3 \cdot CH_2 \cdot C(CH_3)(OH) \cdot COOH$

$1{,}02 \cdot 10^{-4}$	18	$\mathcal{J} = 0{,}01$ bis 0,03	**E2b**	zuv. Weitere Messungen: K_c'-Werte V3.	L11

228 α-Methyl-β-Oxy-n-Buttersäure: $CH_3 \cdot CH(OH) \cdot CH(CH_3) \cdot COOH$

$2{,}25 \cdot 10^{-5}$	18	$\mathcal{J} = 0{,}01$ bis 0,03	**E2b**	rel. zuv.	L10

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
229	Diäthyl-Glykolsäure: $(CH_3{\cdot}CH_2)_2C(OH){\cdot}COOH$					
	$1{,}57{\cdot}10^{-3}$	18	$\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	L11
					Weitere Messungen: K_c-Werte V3.	
230	γ-Oxy-Valeriansäure: $CH_3{\cdot}CH(OH){\cdot}(CH_2)_2{\cdot}COOH$					
	$2{,}06{\cdot}10^{-5}$	18	$\mathcal{J} \geq 0{,}01$	**E2b**	zuv.	L11
231	γ-Oxy-iso-Capronsäure: $CH_3{\cdot}C(CH_3)(OH){\cdot}(CH_2)_2{\cdot}COOH$					
	$1{,}34{\cdot}10^{-5}$	18	$\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	rel. zuv.	L10
232	Glukuronsäure: $CH_2(OH){\cdot}[CH(OH)]_4{\cdot}COOH$					
	K_c $6{,}6{\cdot}10^{-4}$	20				H36
233	ε-Oxy-β-Methyl-ε-iso-Propyl-n-Capronsäure: $CH_3{\cdot}CH(CH_3){\cdot}CH(OH){\cdot}(CH_2)_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}COOH$					
	$8{,}4{\cdot}10^{-6}$	18	$\mathcal{J} = 0{,}1$ bis $0{,}03$	**E2b**	zuv.	L10
234	*trans*-2-Oxy-Cyclohexan-carbonsäure: 					
	$2{,}08{\cdot}10^{-5}$	25	$\mathcal{J} = 0{,}1$	**E2c**	rel. zuv.	K10
235	*cis*-2-Oxy-Cyclohexan-carbonsäure: 					

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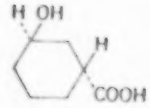
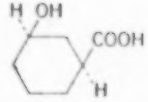
$1{,}60 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}1$	**E2c**	rel. zuv.	K10
				Weitere Messung: K_c-Werte bei 18° V1.	

236 *trans*-3-Oxy-Cyclohexan-carbonsäure:



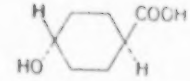
$1{,}53 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}1$	**E2c**	rel. zuv.	K10

237 *cis*-3-Oxy-Cyclohexan-carbonsäure:



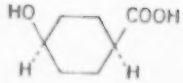
$2{,}50 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}1$	**E2c**	rel. zuv.	K10

238 *trans*-4-Oxy-Cyclohexan-carbonsäure:

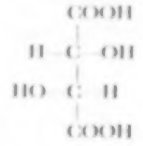


$2{,}10 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}1$	**E2c**	rel. zuv.	K10

239 *cis*-4-Oxy-Cyclohexan-carbonsäure:

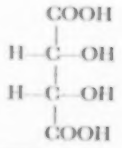


$1{,}46 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}1$	**E2c**	rel. zuv.	K10

No.	*Name, Formel u. Dissoziations-konstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
240	Äpfelsäure: $COOH{\cdot}CH_2{\cdot}CH(OH){\cdot}COOH$					
	K_2 $7{,}25{\cdot}10^{-6}$	25	$\varkappa = 2$ $\mathcal{J} = 0{,}075$ bis $0{,}15$	**E3a** Lösl. mssg. **D2**	unsicher.	L3
					Weitere Messung: K_1-Werte A14.	
241	*d*-Weinsäure: 					
	K_1 $7{,}62{\cdot}10^{-4}$ K_2 $3{,}75{\cdot}10^{-5}$	0	$\mathcal{J} = 0{,}02$ bis $0{,}13$	**E1a**	zuv.	B14
	K_1 $8{,}035{\cdot}10^{-4}$ K_2 $3{,}92{\cdot}10^{-5}$	5				
	K_1 $8{,}414{\cdot}10^{-4}$ K_2 $4{,}08{\cdot}10^{-5}$	10				
	K_1 $8{,}770{\cdot}10^{-4}$ K_2 $4{,}16{\cdot}10^{-5}$	15				
	K_1 $9{,}037{\cdot}10^{-4}$ K_2 $4{,}25{\cdot}10^{-5}$	20				
	K_1 $9{,}205{\cdot}10^{-4}$ K_2 $4{,}31{\cdot}10^{-5}$	25				
	K_1 $9{,}440{\cdot}10^{-4}$ K_2 $4{,}32{\cdot}10^{-5}$	30				
	K_1 $9{,}572{\cdot}10^{-4}$ K_2 $4{,}30{\cdot}10^{-5}$	35				
	K_1 $9{,}594{\cdot}10^{-4}$ K_2 $4{,}25{\cdot}10^{-5}$	40				

	K_1 9,550·10^{-4} K_2 4,17·10^{-5}	45				
	K_1 9,528·10^{-4} K_2 4,06·10^{-5}	50				
	K_1 1,04·10^{-3} K_2 4,55·10^{-5}	25	$\mathcal{J}$ = 0,0016 bis 0,016	**E1b** **R3a**	rel. zuv.	J12
	K_1 1,14·10^{-3} K_2 4,06·10^{-5}	50				
	K_1 0,98·10^{-3} K_2 3,08·10^{-5}	74				
	K_1 1,05·10^{-3} K_2 4,07·10^{-5}	20	$\mathcal{J}$ = 0,1	**E3b** **D1** **R3c**	unsicher.	B39
	K_2 4,05·10^{-5}	18	$\varkappa$ = 1,7 $\mathcal{J}$ = 0,012 bis 0,4	**E3a**	unsicher.	L4
	K_1 1,17·10^{-3} K_2 5,92·10^{-5}	17	$\mathcal{J}$ = 0,03 bis 0,07	**E3a** **D1**	unsicher.	K37
	K_1 0,97·10^{-3} K_2 2,93·10^{-5}	25	$\varkappa$ = 6	**E3a** **D1**	unsicher.	S4
					Weitere Messungen: A14; B52; D7; H2; K28; L3.	

242 *meso*-Weinsäure:



	K_1 6,0·10^{-4} K_2 1,53·10^{-5}	25	$\mathcal{J}$ = 0,0016 bis 0,016	**E1b** **R3a**	zuv.	J5
	K_1 7,3·10^{-4} K_2 1,46·10^{-5}	50				
	K_1 5,2·10^{-4} K_2 1,26·10^{-5}	74				

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	K_1 6,92·10^{-4} K_2 1,26·10^{-5}	20	$\mathcal{J} = 0{,}1$	**E3b** **D1** **R3c**	unsicher.	B39
	K_1 7,75·10^{-4} K_2 1,60·10^{-5}	19	$\mathcal{J} = 0{,}14$	**E3a** **D1**	unsicher.	K37
243	Zitronensäure: COOH·CH_2·C(OH)(COOH)·CH_2·COOH					
	pK_1 3,220 pK_2 4,837 pK_3 6,393	0	$\mathcal{J} \leq 0{,}01$	**E1a** für pK_2 **E1d**	zuv.	B15
	pK_1 3,200 pK_2 4,813 pK_3 6,386	5				
	pK_1 3,176 pK_2 4,797 pK_3 6,383	10				
	pK_1 3,160 pK_2 4,782 pK_3 6,384	15				
	pK_1 3,142 pK_2 4,769 pK_3 6,388	20				
	pK_1 3,128 pK_2 4,761 pK_3 6,396	25				
	pK_1 3,116 pK_2 4,755 pK_3 6,406	30				
	pK_1 3,109 pK_2 4 751 pK_3 6,423	35				
	pK_1 3,099 pK_2 4,750	40				

	pK_3 6,439							
	pK_1 3,097		45					
	pK_2 4,754							
	pK_3 6,462							
	pK_1 3,095		50					
	pK_2 4,757							
	pK_3 6,484							
	K_1 $7{,}49 \cdot 10^{-4}$		25	m = 0,01 bis 0,11	**L1** ähnl. **R1a**	zuv.		L17
				123				
244	Glycin, (Glykokoll), Amino-Essigsäure: $NH_2{\cdot}CH_2{\cdot}COOH$							
	pK_1 2,405		10	$\mathcal{J}$ = 0,01 bis 0,1	**E1a**	sehr zuv.		O6
	2,366		20					
	2,350		25					
	2,338		30					
	2,318		40					
	2,313		45					
	(m) pK_1 (a)	(b) 2,4176	5	$\mathcal{J}$ = 0,01 bis 0,36	(a) **E1a** (b) **E1b**	sehr zuv.		(a) K18 (b) K17
	pK_1 2,3971	2,3980	10					
	pK_2 10,1928							
	pK_1 2,3800	2,3795	15					
	pK_2 10,0439							
	pK_1 2,3640	2,3640	20					
	pK_2 9,9103							
	pK_1 2,3503	2,3508	25					
	pK_2 9,7796							
	pK_1 2,3394	2,3404	30					
	pK_2 9,6517							
	pK_1 2,3312	2,3318	35					
	pK_2 9,5300							
	pK_1 2,3266	2,3252	40					
	pK_2 9,4124							
	pK_1 2,3242	2,3212	45					
	pK_2 9,2988							
	pK_1 2,3200	2,3194	50					
	pK_2 9,1887							
	pK_1	2,3194	55					

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	K_1 $4{,}92 \cdot 10^{-3}$ K_2 $5{,}56 \cdot 10^{-10}$	25	$\mathcal{J} = 0{,}1$ bis 2,7	**E1b**	zuv.	H20
	pK_1 2,41 pK_2 9,75	25	$c = 0{,}1$	**E3b** **D1**	rel. zuv. bis unsicher.	C19
	pK_1 2,365 pK_2 9,715	25	$\mathcal{J} \geq 0{,}005$	**E3a** **D1**	rel. zuv.	S22
	pK_1 2,33 pK_2 9,80	20	$\mathcal{J} \leq 0{,}8$	**E3b** **D1**	rel. zuv. bis unsicher.	G14
					Weitere Messungen: B46; E4; O48.	
245	*N*-Methyl-Glycin: $CH_3 \cdot NH \cdot CH_2 \cdot COOH$					
	pK_1 2,35 pK_2 10,18	25	$c = 0{,}1$	**E3b** **D1**	rel. zuv. bis unsicher.	C19
246	*N*-Äthyl-Glycin: $CH_3 \cdot CH_2 \cdot NH \cdot CH_2 \cdot COOH$					
	pK_1 2,34 pK_2 10,23	25	$c = 0{,}1$	**E3b** **D1**	rel. zuv. bis unsicher.	C19
247	*N*-n-Propyl-Glycin: $CH_3 \cdot (CH_2)_2 \cdot NH \cdot CH_2 \cdot COOH$					
	pK_1 2,35 pK_2 10,19	25	$c = 0{,}1$	**E3b** **D1**	rel. zuv. bis unsicher.	C19
248	*N*-n-Butyl-Glycin: $CH_3 \cdot (CH_2)_3 \cdot NH \cdot CH_2 \cdot COOH$					
	pK_1 2,35 pK_2 10,25	25	$c = 0{,}1$	**E3b** **D1**	rel. zuv. bis unsicher.	C19
249	*N*-iso-Butyl-Glycin: $CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot NH \cdot CH_2 \cdot COOH$					
	pK_1 2,35 pK_2 10,12	25	$c = 0{,}1$	**E3b** **D1**	rel. zuv. bis unsicher.	C19

250	*N*-Formyl-Glycin: $CHO{\cdot}NH{\cdot}CH_2{\cdot}COOH$					
	pK 3,43	19	$\mathcal{J}$ = 0,01 bis 0,03	**E3a**	rel. zuv.	Z1a
251	*N*-Acetyl-Glycin: $CH_3{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$					
	(*m*) pK_1 3,6816	5	$\varkappa$ = 0,3	**E1a**	sehr zuv.	K23
	3,6759	10	$\mathcal{J}$ = 0,025 bis 0,3			
	3,6726	15				
	3,6671	20				
	3,6698	25				
	3,6731	30				
	3,6779	35				
	3,6845	40				
	3,6945	45				
	3,7063	50				
	pK_1 3,685	25	$\mathcal{J}$ = 0,001 bis 0,5	**E3a** **D3**	zuv.	N5
	pK_1 3,61	20	$\mathcal{J}$ = 0,01 bis 0,03	**E3a**	rel. zuv.	Z1a
252	*N*-(β-Chloracetyl)-Glycin: $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$					
	pK_1 3,38	20	$\mathcal{J}$ = 0,01 bis 0,03	**E3a**	rel. zuv.	Z1a
253	*N*-Propionyl-Glycin: $CH_3{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$					
	(*m*) pK_1 3,7284	5	$\varkappa$ = 0,3	**E1a**	sehr zuv.	K23
	3,7225	10	$\mathcal{J}$ = 0,03 bis 0,5			
	3,7184	15				
	3,7164	20				
	3,7176	25				
	3,7208	30				
	3,7253	35				
	3,7310	40				
	3,7402	45				
	3,7502	50				

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254	*N*-Carbamoyl-Glycin: $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$					
	pK_1 3,81	20,3	$\mathcal{J}$ = 0,01 bis 0,03	**E3a**	rel. zuv.	Z1a
	pK_1 3,9107	5	$\mathcal{J}$ = 0,01 bis 0,4	**E1a**	sehr zuv.	K22
	3,8995	10				
	3,8894	15				
	3,8788	20				
	3,8758	25				
	3,8736	30				
	3,8731	35				
	3,8753	40				
	3,8804	45				
	3,8878	50				
255	*N*-Carbäthoxy-Glycin: $CH_3{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$					
	pK_1 3,66	21,8	$\mathcal{J}$ = 0,01 bis 0,03	**E3a**	rel. zuv.	Z1a
256	*N,N*-Di(*β*-oxyäthyl)-Glycin: $(HO{\cdot}CH_2{\cdot}CH_2)_2{\cdot}N{\cdot}CH_2{\cdot}COOH$					
	pK_s 8,08	30	$\mathcal{J}$ = 0,1		unsicher.	C9
257	*dl*-Alanin: $CH_3{\cdot}CH(NH_2){\cdot}COOH$					
	(*m*) pK_1 2,350	20	$\mathcal{J}$ = 0,015 bis 0,22	**E1a**	zuv.	N8
	(*m*) pK_2 10,006					
	pK_1 2,340	25				
	pK_2 9,870					
	pK_1 2,332	30				
	pK_2 9,740					
	pK_1 2,327	35				

	pK_2 9,615					
	pK_1 2,324	40				
	pK_2 9,494					
	pK_1 2,322	45				
	pK_2 9,378					
	(*m*) pK_1 2,420	10	$\mathcal{J}$ = 0,03 bis 0,2	**E1a**	zuv.	S24
	(*m*) pK_2 10,586					
	pK_1 2,383	12,5				
	pK_2 10,225					
	pK_1 2,348	25				
	pK_2 9,866					
	pK_1 2,330	37,5				
	pK_2 9,548					
	pK_1 2,332	50				
	pK_2 9,256					
	pK_1 2,40	25	c = 0,1	**E3b**	rel. zuv. bis unsicher.	C19
	pK_2 9,75			**D1**		
	pK_1 2,31	0		**E3b**	rel. zuv. bis unsicher.	B46
	pK_2 10,47			**D1**		
	pK_1 2,33	20				
	pK_2 9,83					
258	*N*-Methyl-Alanin: $CH_3{\cdot}NH{\cdot}CH(CH_3){\cdot}COOH$					
	pK_1 2,22	25	c = 0,1	**E3b**	rel. zuv. bis unsicher.	C19
	pK_2 10,19			**D1**		
259	*N*-Äthyl-Alanin: $CH_3{\cdot}CH_2{\cdot}NH{\cdot}CH(CH_3){\cdot}COOH$					
	pK_1 2,22	25	c = 0,1	**E3b**	rel. zuv. bis unsicher.	C19
	pK_2 10,22			**D1**		
260	*N*-n-Propyl-Alanin: $CH_3{\cdot}(CH_2)_2{\cdot}NH{\cdot}CH(CH_3){\cdot}COOH$					
	pK_1 2,21	25	c = 0,1	**E3b**	rel. zuv. bis unsicher.	C19
	pK_2 10,19			**D1**		

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
261	*dl*-*N*-Acetyl-Alanin: $CH_3{\cdot}CO{\cdot}NH{\cdot}CH(CH_3){\cdot}COOH$					
	(*m*) pK_1 3,6992	5	$\varkappa = 0{,}3$	**E1a**	sehr zuv.	K23
	3,6992	10	$\bar{\jmath} = 0{,}03$ bis 0,4			
	3,7026	15				
	3,7075	20				
	3,7152	25				
	3,7248	30				
	3,7334	35				
	3,7450	40				
	3,7589	45				
	3,7735	50				
262	*dl*-*N*-Carbamoyl-Alanin: $NH_2{\cdot}CO{\cdot}NH{\cdot}CH(CH_3){\cdot}COOH$					
	(*m*) pK_1 3,8979	5	$\bar{\jmath} = 0{,}01$ bis 0,4	**E1a**	sehr zuv.	K22
	3,8935	10				
	3,8906	15				
	3,8900	20				
	3,8924	25				
	3,8963	30				
	3,9018	35				
	3,9084	40				
	3,9186	45				
	3,9305	50				
263	*β*-Amino-Propionsäure: $NH_2{\cdot}(CH_2)_2{\cdot}COOH$					
	K_1 $2{,}21{\cdot}10^{-4}$	0	$\bar{\jmath} = 0{,}008$ bis 0,08	**E1a**	zuv.	M12
	K_2 $1{,}00{\cdot}10^{-11}$					
	K_1 $2{,}36{\cdot}10^{-4}$	5				
	K_2 $1{,}48{\cdot}10^{-11}$					

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	K_1 2,61·10^{-4} K_2 2,98·10^{-11}	15				
	K_1 2,81·10^{-4} K_2 5,82·10^{-11}	25				
	K_1 2,99·10^{-4} K_2 1,09·10^{-10}	35				
	K_1 3,04·10^{-4} K_2 1,44·10^{-10}	40				
	K_1 2,65·10^{-4} K_2 5,72·10^{-11}	25		**Kat.**	unsicher. Keine Aktivitätskoeffizienten.	O48

264 β-Acetylamino-Propionsäure: $CH_3{\cdot}CO{\cdot}NH{\cdot}(CH_2)_2{\cdot}COOH$

(*m*) pK_1 4,4788	5	$\varkappa = 0{,}3$ $J = 0{,}03$ bis $0{,}4$		**Ela**	sehr zuv.	K23
4,4652	10					
4,4564	15					
4,4488	20					
4,4452	25					
4,4441	30					
4,4434	35					
4,4452	40					
4,4508	45					
4,4572	50					

265 β-Ureido-Propionsäure: $NH_2{\cdot}CO{\cdot}NH{\cdot}(CH_2)_2{\cdot}COOH$

(*m*) pK_1 4,5144	5	$J = 0{,}01$ bis $0{,}4$		**Ela**	sehr zuv.	K22
4,5046	10					
4,4966	15					
4,4896	20					
4,4873	25					
4,4858	30					
4,4859	35					
4,4882	40					
4,4934	45					
4,5004	50					

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
266	*dl*-α-Amino-n-Buttersäure: $CH_3{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$					
	(*m*) pK_1 2,334	10	$\mathcal{I} = 0{,}03$ bis 0,2	**E1a**	zuv.	S24
	pK_2 10,530					
	pK_1 2,310	12,5				
	pK_2 10,180					
	pK_1 2,286	25				
	pK_2 9,830					
	pK_1 2,288	37,5				
	pK_2 9,518					
	pK_1 2,297	50				
	pK_2 9,234					
267	α-Acetylamino-n-Buttersäure: $CH_3{\cdot}CO{\cdot}NH{\cdot}CH(CH_2{\cdot}CH_3){\cdot}COOH$					
	(*m*) pK_1 3,6924	5	$\varkappa = 0{,}3$	**E1a**	sehr zuv.	K23
	3,6943	10	$\mathcal{I} = 0{,}03$ bis 0,16			
	3,6986	15				
	3,7059	20				
	3,7158	25				
	3,7262	30				
	3,7375	35				
	3,7502	40				
	3,7667	45				
	3,7822	50				
268	α-Ureido-n-Buttersäure: $NH_2{\cdot}CO{\cdot}NH{\cdot}CH(CH_2{\cdot}CH_3){\cdot}COOH$					
	(*m*) pK_1 3,8774	5	$\mathcal{I} = 0{,}01$ bis 0,4	**E1a**	sehr zuv.	K22
	3,8761	10				
	3,8776	15				
	3,8797	20				
	3,8856	25				

	3,8932	30				
	3,9011	35				
	3,9104	40				
	3,9240	45				
	3,9382	50				

269 γ-Amino-n-Buttersäure: $NH_2 \cdot (CH_2)_3 \cdot COOH$

	pK_1 4,0571	10	J = 0,02 bis 0,15	**EIa**	sehr zuv.	K21
	pK_2 11,0263					
	pK_1 4,0459	15				
	pK_2 10,8674					
	pK_1 4,0380	20				
	pK_2 10,7057					
	pK_1 4,0312	25				
	pK_2 10,5557					
	pK_1 4,0266	30				
	pK_2 10,4091					
	pK_1 4,0251	35				
	pK_2 10,2694					
	pK_1 4,0272	40				
	pK_2 10,1336					
	pK_1 4,0293	45				
	pK_2 10,0025					
	pK_1 4,0320	50				
	pK_2 9,8740					

270 γ-Ureido-n-Buttersäure: $NH_2 \cdot CO \cdot NH \cdot (CH_2)_3 \cdot COOH$

(*m*)	pK_1 4,6938	5	J = 0,01 bis 0,4	**EIa**	sehr zuv.	K22
	4,6873	10				
	4,6838	15				
	4,6820	20				
	4,6831	25				
	4,6848	30				
	4,6887	35				
	4,6941	40				
	4,7028	45				
	4,7134	50				

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
271	α-Amino-iso-Buttersäure: $(CH_3)_2C(NH_2)\cdot COOH$					
	pK_1 2,418 pK_2 10,960	10	$J = 0{,}03$ bis 0,2	**E1a**	zuv.	S24
	pK_1 2,380 pK_2 10,580	12,5				
	pK_1 2,357 pK_2 10,205	25				
	pK_1 2,309 pK_2 9,872	37,5				
	pK_1 2,313 pK_2 9,561	50				
272	α-Ureido-iso-Buttersäure: $NH_2\cdot CO\cdot NH\cdot C(CH_3)_2\cdot COOH$					
	(*m*) pK_1 4,4904	5	$J = 0{,}01$ bis 0,4	**E1a**	sehr zuv.	K22
	4,4805	10				
	4,4726	15				
	4,4635	20				
	4,4627	25				
	4,4612	30				
	4,4603	35				
	4,4627	40				
	4,4667	45				
	4,4742	50				
273	*dl*-α-Amino-n-Valeriansäure: $CH_3\cdot(CH_2)_2\cdot CH(NH_2)\cdot COOH$					
	K_1 $4{,}4\cdot10^{-5}$ K_2 $1{,}9\cdot10^{-10}$	25		**E3b**	unsicher. Nähere Angaben fehlen.	S10
	(*m*) pK_1 2,376 (*m*) pK_2 10,508	0	$J = 0{,}02$ bis 0,2	**E1a**	zuv.	S24

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	pK_1 2,340	12,5				
	pK_2 10,154					
	pK_1 2,318	25				
	pK_2 9,808					
	pK_1 2,309	37,5				
	pK_2 9,490					
	pK_1 2,313	50				
	pK_2 9,178					
274	*β*-Amino-n-Valeriansäure: $CH_3{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}COOH$					
	K_1 $9{,}5{\cdot}10^{-5}$	25		**E3b**	unsicher.	S10
	K_2 $3{,}99{\cdot}10^{-11}$				Nähere Angaben fehlen.	
275	*δ*-Amino-n-Valeriansäure: $NH_2{\cdot}(CH_2)_4{\cdot}COOH$					
	K_1 $6{,}3{\cdot}10^{-5}$	25		**E3b**	unsicher.	S10
	K_2 $2{,}04{\cdot}10^{-11}$				Nähere Angaben fehlen.	
	pK_1 4,270	25	$\mathcal{J}$ = 0,004 bis 0,5	**E3a**	zuv.	N5
	pK_2 10,766			**D3**		
					Weitere Messungen: O48	
276	*dl*-Valin: $(CH_3)_2CH{\cdot}CH(NH_2){\cdot}COOH$					
	(*m*) pK_1 2,320	0	$\mathcal{J}$ = 0,02 bis 0,2	**E1a**	zuv.	S24
	(*m*) pK_2 10,431					
	pK_1 2,297	12,5				
	pK_2 10,664					
	pK_1 2,286	25				
	pK_2 9,744					
	pK_1 2,292	37,5				
	pK_2 9,434					
	pK_1 2,310	50				
	pK_2 9,142					
					Weitere Messungen: S10	

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
277	*dl*-Norleucin: $CH_3{\cdot}(CH_2)_3{\cdot}CH(NH_2){\cdot}COOH$					
	(*m*) pK_1 2,394 (*m*) pK_2 10,564	0	$\mathcal{J}$ = 0,02 bis 0,2	**E1a**	zuv.	S24
	pK_1 2,356 pK_2 10,190	12,5				
	pK_1 2,335 pK_2 9,834	25				
	pK_1 2,324 pK_2 9,513	37,5				
	pK_1 2,328 pK_2 9,224	50				
					Weitere Messungen: S10	
278	ε-Amino-n-Capronsäure: $NH_2{\cdot}(CH_2)_5{\cdot}COOH$					
	pK_1 4,43 pK_2 10,75	25,1	$\mathcal{J}$ = 0,04	**E3b** **D1**	K_c-Werte; unsicher.	E1
279	*dl*-Leucin: $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 2,383 pK_2 10,454	10	$\mathcal{J}$ = 0,03 bis 0,2	**E1a**	zuv.	S24
	pK_1 2,348 pK_2 10,095	12,5				
	pK_1 2,328 pK_2 9,744	25				
	pK_1 2,327 pK_2 9,434	37,5				
	pK_1 2,333 pK_2 9,142	50				
	pK_2 9,74	18	$\mathcal{J}$=0,01	**E3b** **D1**	unsicher.	M17

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280 *l*-Leucin: 25 $\mathcal{I} \simeq 0{,}1$

pK_2 9,68			unsicher. ($Kf_A - If_{HA}$)-Werte nach **E3b**; nur f_{H^+} berücksichtigt.	E4
			Weitere Messungen: E4	

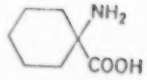
281 *dl*-Isoleucin: $CH_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH(NH_2){\cdot}COOH$

pK_1 2,365 pK_2 10,460	0	$\mathcal{I}$ = 0,03 bis 0,2	**E1a** zuv.	S24
pK_1 2,338 pK_2 10,100	12,5			
pK_1 2,318 pK_2 9,758	25			
pK_1 2,317 pK_2 9,439	37,5			
pK_1 2,332 pK_2 9,157	50			
			Weitere Messungen: *d*-Isoleucin: S10.	

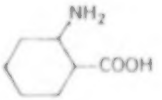
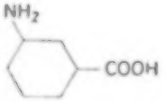
282 ω-Amino-n-Dodecansäure: $NH_2{\cdot}(CH_2)_{11}{\cdot}COOH$

pK_1 4,648	25	$\mathcal{I}$ = 0,004 bis 0,5	**E3a** **D3** zuv.	N5

283 1,1-Amino-Cyclohexan-carbonsäure:



K_1 $2{,}21 \cdot 10^{-3}$ K_2 $9{,}33 \cdot 10^{-11}$	25	**Kat.**	unsicher. Keine Aktivitätskoeffizienten.	O4a

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
284	1,2-Amino-Cyclohexan-carbonsäure: 					
	K_1 2,58·10^{-4} K_2 6,18·10^{-11}	25		**Kat.**	unsicher. Keine Aktivitätskoeffizienten.	O4a
	pK_1 3,4 pK_2 10,1	fehlt		**E3b**	unsicher.	G19
285	1,3-Amino-Cyclohexan-carbonsäure: 					
	K_1 9,96·10^{-5} K_2 3,12·10^{-11}	25		**Kat.**	unsicher. Keine Aktivitätskoeffizienten.	O4a
	pK_1 4,2 pK_2 10,5	fehlt		**E3b**	unsicher. Keine näheren Angaben.	G19
286	1,3-*trans*-Amino-Cyclohexan-carbonsäure: Formel wie vorhergehend					
	pK_1 3,85	15		**E**	unsicher. Keine näheren Angaben.	H35

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287 1,3-*cis*-Amino-Cyclohexan-carbonsäure: Formel wie vorhergehend

pK_1 3,70	15	**E**	unsicher. Keine näheren Angaben.	H35

288 1,4-Amino-Cyclohexan-carbonsäure:

pK_1 4,3 pK_2 10,5		**E3b**	unsicher. Keine näheren Angaben.	G19

289 1,4-*trans*-Amino-Cyclohexan-carbonsäure: Formel wie vorhergehend

K_1 $4{,}09 \cdot 10^{-5}$ K_2 $2{,}81 \cdot 10^{-11}$	25	**Kat.**	unsicher. Keine Aktivitätskoeffizienten.	O1a

290 1,4-*cis*-Amino-Cyclohexan-carbonsäure: Formel wie vorhergehend

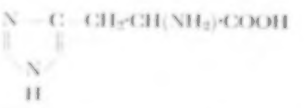
K_1 $1{,}49 \cdot 10^{-5}$ K_2 $2{,}40 \cdot 10^{-11}$	25	**Kat.**	unsicher. Keine Aktivitätskoeffizienten.	O1a

291 Ornithin: $NH_2 \cdot (CH_2)_3 \cdot CH(NH_2) \cdot COOH$

pK_1 1,94 pK_2 8,65 pK_3 10,76	25	**E3b**	unsicher. Die Aktivitätskoeffizienten wurden gleichgesetzt mit denen der Essigsäure.	S10

292 Arginin: $NH{:}C(NH_2) \cdot NH \cdot (CH_2)_3 \cdot CH(NH_2) \cdot COOH$

pK_1 2,24 pK_2 9,79 pK_3 13,31	0	**E3b**	unsicher. Keine näheren Angaben.	S11
pK_1 2,02 pK_2 9,04 pK_3 12,48	25			

No.	Name, Formel u. Dissoziations-Konstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
	(*l*) pK_1 2,10 pK_2 9,07	25	$\mathcal{J} = 0{,}1$	**E3b**	unsicher. (Kf_A^-/f_{HA})-Werte; nur f_{H^+} berücksichtigt.	E4
	pK_1 2,17 pK_2 9,29 $pK_3 > 13{,}2$	17		**E3b** **D1**	unsicher.	B37a
	pK_1 2,18 pK_2 9,09 pK_3 13,2	23				
293	Histidin: 					
	pK_1 2,76 pK_2 6,83 pK_3 9,75	0		**E3b**	unsicher. Keine näheren Angaben.	S11
	pK_1 1,82 pK_2 6,04 pK_3 9,12	25				
	pK_1 1,77 pK_2 6,10 pK_3 9,18	25	$\epsilon = 0{,}02$	**E3b** **D1**	unsicher.	G17
	pK_2 6,12 pK_3 9,17	25	$\mathcal{J} \simeq 0{,}1$	**E3b**	unsicher. K_c-Werte; nur f_{H^+} berücksichtigt.	E4
	pK_1 1,78 pK_2 5,97 pK_3 8,97	23	$\epsilon = 0{,}1$	**E3b** **D1**	unsicher.	B37a

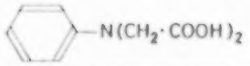
294	*l*-Citrullin: $NH_2{\cdot}CO{\cdot}NH{\cdot}(CH_2)_3{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 2,43 pK_2 9,41	25	$\mathcal{I} \simeq 0{,}1$	**E3b**	unsicher. K_c-Werte; nur f_{H^+} berücksichtigt.	E4
295	Lysin: $NH_2{\cdot}(CH_2)_4{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 3,12 pK_2 9,81 pK_3 11,30	0		**E3b**	unsicher. Keine näheren Angaben.	S11
	pK_1 2,18 pK_2 8,95 pK_3 10,53	25				
	(*l*) pK_1 2,16 pK_2 9,18 pK_3 10,79	25	$\mathcal{I} \simeq 0{,}1$	**E3b**	unsicher. K_c-Werte; nur f_{H^+} berücksichtigt.	E4
	(*d*) pK_1 2,15 pK_2 9,16 pK_3 10,81	25	$\mathcal{I} \simeq 0{,}1$	**E3b**	unsicher. K_c-Werte; nur f_{H^+} berücksichtigt.	E4
296	Asparaginsäure: $COOH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 2,10 pK_2 3,86 pK_3 9,82	25	$c = 0{,}02$	**E3b** **D1**	unsicher.	G17
	pK_1 2,01 pK_2 3,77 pK_3 10,30	0		**E3b**	unsicher. Keine näheren Angaben.	S11
	pK_1 1,91 pK_2 3,63 pK_3 9,47	25				
	pK_1 2,05 pK_2 3,87 pK_3 10,00	25	$\mathcal{I} \geq 0{,}005$	**E3b** **D1**	rel. zuv.	S22
	pK_2 3,68 pK_3 9,46	30	$\mathcal{I} = 0{,}1$	**E3b**	unsicher.	G10

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
297	Asparagin: $NH_2{\cdot}CO{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 8,82	18	$\mathcal{J} \simeq 0{,}01$	**E3b** **D1**	unsicher.	M17
298	Glutaminsäure: $COOH{\cdot}(CH_2)_2{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 2,23 pK_2 4,14 pK_3 10,22	0		**E3b**	unsicher. Keine näheren Angaben.	S11
	pK_1 2,10 pK_2 4,07 pK_3 9,47	25		**E3b**	unsicher. Die Aktivitätskoeffizienten wurden gleichgesetzt mit denen der Essigsäure.	S10
	pK_1 2,155 pK_2 4,324 pK_3 9,960	20	$\mathcal{J} = 0{,}008$ bis $0{,}18$	**E3a**	unsicher. Nähere experimentelle Angaben fehlen.	N4
299	Glutaminsäure-α-Äthylhalbester: $COOH{\cdot}(CH_2)_2{\cdot}CH(NH_2){\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_3$					
	pK_1 3,846 pK_2 7,838		$\mathcal{J} = 0{,}004$ bis $0{,}05$	**E3a**	unsicher. Ohne experimentelle Angaben.	N4
300	Glutaminsäure-γ-Äthylhalbester: $CH_3{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}(CH_2)_2{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 2,148 pK_2 9,19		$\mathcal{J} = 0{,}008$ bis $0{,}244$	**E3a**	unsicher. Ohne experimentelle Angaben.	N4
301	Imino-Diessigsäure: $COOH{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}COOH$					
	pK_1 2,54 pK_2 9,12	30	$\mathcal{J} = 0{,}1$	**E3b** u. **E1c**	unsicher.	C10

302 Methylamin-Diessigsäure: $COOH{\cdot}CH_2{\cdot}N(CH_3){\cdot}CH_2{\cdot}COOH$

pK_1 2,138 pK_2 10,474	0	$\mathcal{J} = 0{,}03$ bis $0{,}15$	**E1a**	sehr zuv.	O1
pK_1 2,142 pK_2 10,287	10				
pK_1 2,146 pK_2 10,088	20				
pK_1 2,150 pK_2 9,920	30				
pK_1 2,154 pK_2 9,763	40				

303 Anilin-Diessigsäure:



pK_1 2,40 pK_2 4,98	20	$\mathcal{J} \simeq 0{,}1$	**E1d** Graph. Auswertung	unsicher. K_c-Werte bei $\mathcal{J} \simeq 0{,}1$	S11b
				Weitere Messungen an Derivaten der Säure.	

304 Nitrilo-Essigsäure: $N(CH_2{\cdot}COOH)_3$

pK_2 2,956 pK_3 10,230	30			unsicher. nähere Angaben fehlen.	O1

305 Imino-Propionsäure-Essigsäure: $COOH{\cdot}(CH_2)_2{\cdot}NH{\cdot}CH_2{\cdot}COOH$

pK_1 3,61 pK_2 9,46	30	$\mathcal{J} = 0{,}1$	**E3b**	unsicher.	C11

306 Imino-Dipropionsäure: $COOH{\cdot}(CH_2)_2{\cdot}NH{\cdot}(CH_2)_2{\cdot}COOH$

pK_1 4,11 pK_2 9,61	30	$\mathcal{J} = 0{,}1$	**E3b** u. **E1c**	unsicher.	C10

307 Äthylendiamin-*N*,*N*'-Diessigsäure: $COOH{\cdot}CH_2{\cdot}NH{\cdot}(CH_2)_2{\cdot}NH{\cdot}CH_2{\cdot}COOH$

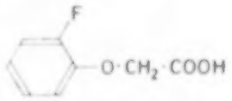
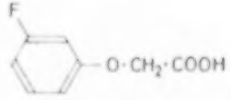
pK_1 6,42 pK_2 9,46	30	$\mathcal{J} = 0{,}1$	**E3b** u. **E1c**	unsicher.	C12

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
308	Äthylendiamin-*N*-Dimethyl-*N'*-Diessigsäure: $(CH_3)_2N{\cdot}(CH_2)_2{\cdot}N(CH_2{\cdot}COOH)_2$					
	pK_1 6,294 pK_2 10,446	0	J = 0,03 bis 0,15	**E1a**	sehr zuv.	O1
	pK_1 6,169 pK_2 10,268	10				
	pK_1 6,047 pK_2 10,068	20				
	pK_1 5,926 pK_2 9,882	30				
	pK_1 5,803 pK_2 9,684	40				
309	Äthylendiamin-*N,N'*-Tetraessigsäure: $(COOH{\cdot}CH_2)_2N{\cdot}(CH_2)_2{\cdot}N(CH_2{\cdot}COOH)_2$					
	pK_3 6,47 pK_4 10,1	25	J = 0,03 bis 1	**E3b** u. **E1c**	unsicher.	C1
	pK_3 6,527 pK_4 11,308	0	J = 0,005 bis 0,1	**E1a**	sehr zuv.	C2
	pK_3 6,476 pK_4 11,234	5				
	pK_3 6,425 pK_4 11,159	10				
	pK_3 6,369 pK_4 11,084	15				
	pK_3 6,320 pK_4 11,014	20				
	pK_3 6,273 pK_4 10,948	25				
	pK_3 6,236 pK_4 10,883	30				

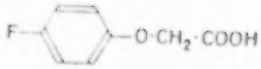
310	Äthylendiamin-*N,N'*-Dipropionsäure-*N,N'*-Diessigsäure: $COOH{\cdot}(CH_2)_2{\cdot}N(CH_2{\cdot}COOH){\cdot}(CH_2)_2{\cdot}N(CH_2{\cdot}COOH){\cdot}(CH_2)_2{\cdot}COOH$					
	pK_1 3,00 pK_2 3,79 pK_3 5,98 pK_4 9,83	30	$\mathcal{J} = 0{,}1$	**E3b** u. **E1c**	unsicher.	G12
311	Äthylendiamin-*N,N'*-Dipropionsäure: $COOH{\cdot}(CH_2)_2{\cdot}NH{\cdot}(CH_2)_2{\cdot}NH{\cdot}(CH_2)_2{\cdot}COOH$					
	pK_1 6,87 pK_2 9,60	30	$\mathcal{J} = 0{,}1$	**E3b**	unsicher.	G23
312	Äthylendiamin-*N-N'*-Tetrapropionsäure: $(COOH{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}(CH_2)_2{\cdot}N(CH_2{\cdot}CH_2{\cdot}COOH)_2$					
	pK_1 3,00 pK_2 3,43 pK_3 6,77 pK_4 9,60	30	$\mathcal{J} = 0{,}1$	**E3b**	unsicher.	G23
	Di- und Polypeptide—meist K_s-Werte oder gemischte Konstanten—sind u.a. zu finden bei: B46; E4; G14; G17; G18; G20; L18; N5; P10					
	124					
313	Brenztraubensäure: $CH_3{\cdot}CO{\cdot}COOH$					
	$3{,}24{\cdot}10^{-3}$ 3,80	25 37		**E3b** **D2**	rel. zuv.	P5
	$1{,}78{\cdot}10^{-3}$	18	$\mathcal{J} = 0{,}01$ bis 0,03	**E2b**	rel. zuv.	L10
314	Acetessigsäure: $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH$					
	$2{,}57{\cdot}10^{-4}$ 2,62	0 18	$\mathcal{J} \geq 0{,}05$	**E2c** **D1**	unsicher. Säure zersetzt sich.	D4
	$2{,}2{\cdot}10^{-4}$	18	$\mathcal{J} = 0{,}02$ bis 0,03	**E2b**	unsicher. Säure zersetzt sich.	L10
315	Lävulinsäure: $CH_3{\cdot}CO{\cdot}(CH_2)_2{\cdot}COOH$					
	$2{,}30{\cdot}10^{-5}$	18	$\mathcal{J} = 0{,}01$ bis 0,03	**E2b**	zuv.	L11

No.	*Name, Formel u. Dissoziations-konstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
316	α,γ-Diketo-n-Valeriansäure: $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}COOH$					
	K_1 $2{,}6{\cdot}10^{-3}$ K_2 $3{,}2{\cdot}10^{-9}$	25	$\varepsilon = 0{,}0485$ $\varepsilon = 0{,}0325$	**E3a**	unsicher. Wenig exper. Angaben	L15
317	γ-Acetyl-n-Buttersäure: $CH_3{\cdot}CO{\cdot}(CH_2)_2{\cdot}COOH$					
	$2{,}18{\cdot}10^{-5}$	18	$\bar{f} = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	L10
318	Oxalessigsäure: $COOH{\cdot}CH_2{\cdot}CO{\cdot}COOH$					
	K_1 $2{,}79{\cdot}10^{-3}$ K_2 $4{,}27{\cdot}10^{-5}$	25		**E3b** **D2**	zuv.	P5
	K_1 $3{,}55{\cdot}10^{-3}$ K_2 $4{,}38{\cdot}10^{-5}$	37				

125

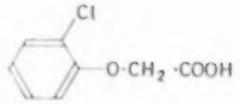
319	*o*-Fluorphenoxy-Essigsäure: 					
	$8{,}22{\cdot}10^{-4}$	25	$\varepsilon = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29
320	*m*-Fluorphenoxy-Essigsäure: 					
	$8{,}28{\cdot}10^{-4}$	25	$\varepsilon = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29

321 *p*-Fluorphenoxy-Essigsäure:



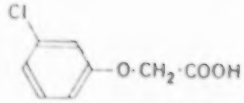
$7{,}42 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29

322 *o*-Chlorphenoxy-Essigsäure:



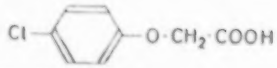
$8{,}90 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29

323 *m*-Chlorphenoxy-Essigsäure:



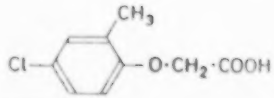
$8{,}51 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29

324 *p*-Chlorphenoxy-Essigsäure:

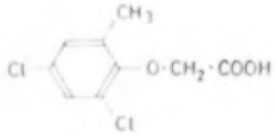
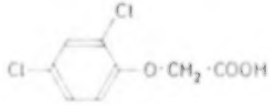
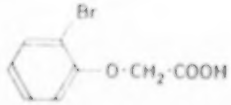


$7{,}89 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29

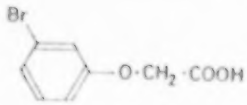
325 2-Methyl-4-Chlorphenoxy-Essigsäure:



$5{,}2 \cdot 10^{-4}$			**L**	unsicher. Ohne nähere Angaben.	K1

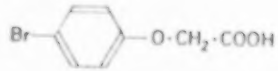
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
326	2-Methyl-4,6-Dichlorphenoxy-Essigsäure: 					
	$7{,}4 \cdot 10^{-4}$			**L**	unsicher. Ohne nähere Angaben.	K1
327	2,4-Dichlorphenoxy-Essigsäure: 					
	$2{,}3 \cdot 10^{-3}$			**L**	unsicher. Ohne nähere Angaben.	K1
328	*o*-Bromphenoxy-Essigsäure: 					
	$7{,}53 \cdot 10^{-4}$	25	$\epsilon = 0{,}008$ bis 0,1	**E1a**	zuv.	H29

329 *m*-Bromphenoxy-Essigsäure:



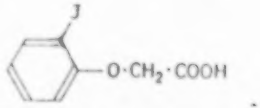
$8{,}03 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**Ela**	zuv.	H29

330 *p*-Bromphenoxy-Essigsäure:



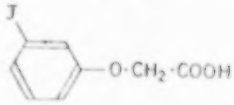
$7{,}37 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**Ela**	zuv.	H29

331 *o*-Jodphenoxy-Essigsäure:



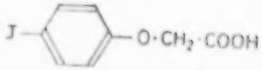
$6{,}72 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**Ela**	zuv.	H29

332 *m*-Jodphenoxy-Essigsäure:

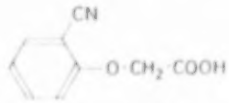
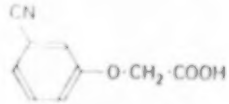
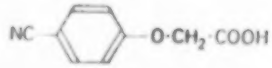
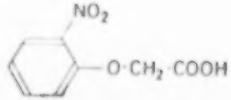


$7{,}44 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**Ela**	zuv.	H29

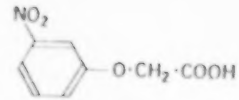
333 *p*-Jodphenoxy-Essigsäure:



$6{,}94 \cdot 10^{-4}$	25	$c = 0{,}008$ bis $0{,}1$	**Ela**	zuv.	H29

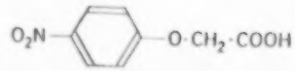
No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
334	*o*-Cyanphenoxy-Essigsäure: 					
	$1{,}06 \cdot 10^{-3}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29
335	*m*-Cyanphenoxy-Essigsäure: 					
	$0{,}924 \cdot 10^{-3}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29
336	*p*-Cyanphenoxy-Essigsäure: 					
	$1{,}17 \cdot 10^{-3}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29
337	*o*-Nitrophenoxy-Essigsäure: 					
	$1{,}27 \cdot 10^{-3}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29

338 *m*-Nitrophenoxy-Essigsäure:



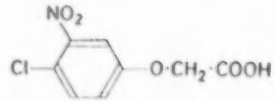
$1{,}12 \cdot 10^{-3}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29

339 *p*-Nitrophenoxy-Essigsäure:



$1{,}28 \cdot 10^{-3}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29

340 3-Nitro-4-Chlor-phenoxy-Essigsäure:



$1{,}10 \cdot 10^{-3}$	25	$c = 0{,}008$ bis $0{,}1$	**E1a**	zuv.	H29

341 Dimilchsäure: $CH_3 \cdot CH(OH) \cdot CO \cdot O \cdot CH(CH_3) \cdot COOH$

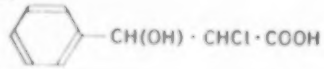
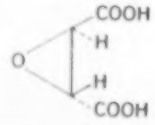
$1{,}11 \cdot 10^{-3}$	22	$c = 0{,}014$ bis $0{,}14$	**E3a** **D1**	unsicher.	B31

342 *β*-Chlor-Milchsäure: $CH_2Cl \cdot CH(OH) \cdot COOH$

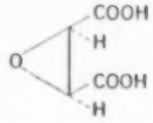
$7{,}6 \cdot 10^{-4}$	25		**L2**	unsicher. K_c'-Werte.	S23

343 *α*-Chlor-*β*-Oxy-n-Buttersäure: $CH_3 \cdot CH(OH) \cdot CHCl \cdot COOH$

$2{,}6 \cdot 10^{-3}$	25		**L2**	unsicher. K_c'-Werte.	S23

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
344	α-Oxy-β-Chlor-n-Buttersäure: $CH_3 \cdot CHCl \cdot CH(OH) \cdot COOH$					
	$8{,}24 \cdot 10^{-4}$	25		**L2**	unsicher. K_c-Werte.	S23
345	α-Oxy-β-Chlor-iso-Buttersäure: $CH_2Cl \cdot C(CH_3)(OH) \cdot COOH$					
	$6{,}30 \cdot 10^{-4}$	25		**L2**	unsicher. K_c-Werte.	S23
346	α-Oxy-α′-Chlor-Bernsteinsäure: $COOH \cdot CHCl \cdot CH(OH) \cdot COOH$					
	$4{,}8 \cdot 10^{-3}$	25		**L2**	unsicher. K_c-Werte.	S23
347	Acetyl-Zitronensäure: $CH_3 \cdot CO \cdot O \cdot C(CH_2 \cdot COOH)_2 \cdot COOH$					
	$3{,}20 \cdot 10^{-3}$	25		**L2**	unsicher. K_c-Werte.	S23
348	α-Chlor-β-Oxy-β-Phenyl-Propionsäure: 					
	$2{,}48 \cdot 10^{-3}$	25		**L2**	unsicher. K_c-Werte.	S23
349	*trans*-Äthylenoxyd-dicarbonsäure: 					
	K_1 $1{,}18 \cdot 10^{-2}$ K_2 $5{,}62 \cdot 10^{-4}$	19	$\mathcal{J} = 0{,}12$	**E3a** **D1**	unsicher.	W4

350 *cis*-Äthylenoxyd-dicarbonsäure:



K_1 1,15·10^{-2} K_2 1,20·10^{-4}	18	$\mathcal{J} = 0{,}12$	**E3a** **D1**	unsicher.	W5

351 Malonsäure-Monoamid: $NH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH$

2,284·10^{-4}	25	$c = 0{,}0001$ bis $0{,}01$	**L1** **R1b** **K2d**	zuv. Parker-Effekt möglich.	J5

352 Bernsteinsäure-Monoamid: $NH_2{\cdot}CO{\cdot}(CH_2)_2{\cdot}COOH$

2,892·10^{-5}	25	$c = 0{,}001$ bis $0{,}01$	**L1** **R1b** **K2d**	zuv. Parker-Effekt möglich.	J5

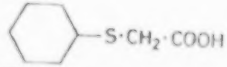
353 Glutarsäure-Monoamid: $NH_2{\cdot}CO{\cdot}(CH_2)_3{\cdot}COOH$

2,510·10^{-5}	25	$c = 0{,}001$ bis $0{,}01$	**L1** **R1b** **K2d**	zuv. Parker-Effekt möglich.	J5

354 Adipinsäure-Monoamid: $NH_2{\cdot}CO{\cdot}(CH_2)_4{\cdot}COOH$

2,352·10^{-5}	25	$c = 0{,}001$ bis $0{,}01$	**L1** **R1b** **K2d**	zuv. Parker-Effekt möglich.	J5

355 Cyclohexyl-thio-Essigsäure:



3,25·10^{-4}	25		**L**	unsicher. ohne nähere Angaben.	M28 M29

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
356	Thio-Diessigsäure: $COOH{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}COOH$					
	K_1 $5{,}01{\cdot}10^{-4}$	18	$\varkappa = 0{,}7$ bis 2	**E3b**	rel. zuv.	A7
	K_2 $3{,}16{\cdot}10^{-5}$		$\mathcal{J} \leq 0{,}1$	**D3**		
	K_2 $3{,}5{\cdot}10^{-5}$	18	$\varkappa = 1{,}5$ bis 2	**E3a**	unsicher.	L4
			$\mathcal{J} = 0{,}04$ bis 0,4	**D2**	$\log f_i = A\sqrt{\mathcal{J}}$.	
357	Dithio-Diessigsäure: $COOH{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}COOH$					
	K_1 $8{,}41{\cdot}10^{-4}$	18	$\varkappa = 0{,}7$ bis 2	**E3b**	rel. zuv.	A7
	K_2 $6{,}30{\cdot}10^{-5}$		$\mathcal{J} \leq 0{,}1$	**D3**		
358	Methylen-bis-thio-Essigsäure: $COOH{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}COOH$					
	K_1 $4{,}90{\cdot}10^{-4}$	18	$\varkappa = 0{,}7$ bis 2	**E3b**	rel. zuv.	A7
	K_2 $4{,}52{\cdot}10^{-5}$		$\mathcal{J} \leq 0{,}1$	**D3**		
359	Äthylen-bis-thio-Essigsäure: $COOH{\cdot}CH_2{\cdot}S{\cdot}(CH_2)_2{\cdot}S{\cdot}CH_2{\cdot}COOH$					
	K_1 $4{,}15{\cdot}10^{-4}$	18	$\varkappa = 0{,}7$ bis 2	**E3b**	rel. zuv.	A7
	K_2 $4{,}45{\cdot}10^{-5}$		$\mathcal{J} \leq 0{,}1$	**D3**		
360	Trimethylen-bis-thio-Essigsäure: $COOH{\cdot}CH_2{\cdot}S{\cdot}(CH_2)_3{\cdot}S{\cdot}CH_2{\cdot}COOH$					
	K_1 $3{,}67{\cdot}10^{-4}$	18	$\varkappa = 0{,}7$ bis 2	**E3b**	rel. zuv.	A7
	K_2 $4{,}14{\cdot}10^{-5}$		$\mathcal{J} \leq 0{,}1$	**D3**		
361	Tetramethylen-bis-thio-Essigsäure: $COOH{\cdot}CH_2{\cdot}S{\cdot}(CH_2)_4{\cdot}S{\cdot}CH_2{\cdot}COOH$					
	K_1 $3{,}44{\cdot}10^{-4}$	18	$\varkappa = 0{,}7$ bis 2	**E3b**	rel. zuv.	A7
	K_2 $3{,}78{\cdot}10^{-5}$		$\mathcal{J} = 0{,}1$	**D3**		
362	Pentamethylen-bis-thio-Essigsäure: $COOH{\cdot}CH_2{\cdot}S{\cdot}(CH_2)_5{\cdot}S{\cdot}CH_2{\cdot}COOH$					
	K_1 $3{,}27{\cdot}10^{-4}$	18	$\varkappa = 0{,}7$ bis 2	**E3b**	rel. zuv.	A7
	K_2 $3{,}86{\cdot}10^{-5}$		$\mathcal{J} \leq 0{,}1$	**D3**		

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363 α-Thio-Propionsäure-Essigsäure: $COOH{\cdot}CH(CH_3){\cdot}S{\cdot}CH_2{\cdot}COOH$

K_2 2,9·10⁻⁵	18	$\varkappa$ = 1,5 bis 2 $\mathcal{J}$ = 0,02 bis 0,2	**E3a** **D2**	unsicher.	L2

364 α-(Methyl-thio)-Propionsäure: $CH_3{\cdot}S{\cdot}CH(CH_3){\cdot}COOH$

1,73·10⁻⁴	25		**L2**	unsicher. Ohne nähere Angaben.	M16

365 α-(Äthyl-thio)-Propionsäure: $CH_3{\cdot}CH_2{\cdot}S{\cdot}CH(CH_3){\cdot}COOH$

1,60·10⁻⁴	25		**L2**	unsicher. Ohne nähere Angaben.	M16

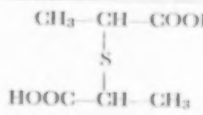
366 α-(n-Propyl-thio)-Propionsäure: $CH_3{\cdot}(CH_2)_2{\cdot}S{\cdot}CH(CH_3){\cdot}COOH$

1,53·10⁻⁴	25		**L2**	unsicher. Ohne nähere Angaben.	M16

367 α-(iso-Propyl-thio)-Propionsäure: $(CH_3)_2CH{\cdot}S{\cdot}CH(CH_3){\cdot}COOH$

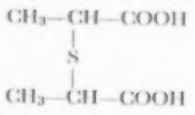
1,67·10⁻⁴	25		**L2**	unsicher. Ohne nähere Angaben.	M16

368 *rac.*-α-Thio-Dipropionsäure:

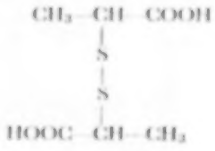
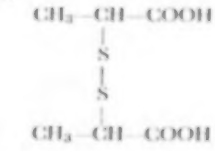


K_2 2,4·10⁻⁵	18	$\varkappa$ = 1,5 bis 2 $\mathcal{J}$ = 0,02 bis 0,2	**E3a** **D2**	unsicher.	L2

369 *meso*-α-Thio-Dipropionsäure:



K_2 2,7·10⁻⁵	18	$\varkappa$ = 1,5 bis 2 $\mathcal{J}$ = 0,01 bis 0,2	**E3a** **D2**	unsicher.	L2

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
370	*rac.*-α-Dithio-Dipropionsäure: 					
	K_1 $7{,}0 \cdot 10^{-4}$	25		**L1**	unsicher. Ohne nähere Angaben.	F4
371	*meso*-α-Dithio-Dipropionsäure: 					
	K_1 $7{,}3 \cdot 10^{-4}$	25		**L1**	unsicher. Ohne nähere Angaben.	F4
372	α-Methylen-bis-thio-Propionsäure: $COOH{\cdot}CH(CH_3){\cdot}S{\cdot}CH_2{\cdot}S{\cdot}CH(CH_3){\cdot}COOH$					
	K_1 $4{,}2 \cdot 10^{-4}$	25		**L1**	unsicher. Ohne nähere Angaben. An Platinelektrode zersetzlich.	F5
373	β-Thio-Dipropionsäure: $COOH{\cdot}(CH_2)_2{\cdot}S{\cdot}(CH_2)_2{\cdot}COOH$					
	K_1 $8{,}22 \cdot 10^{-5}$ K_2 $8{,}41 \cdot 10^{-6}$	18	$\varkappa = 0{,}7$ bis 2 $J = 0{,}1$	**E3b** **D3**	rel. zuv.	A7

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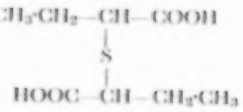
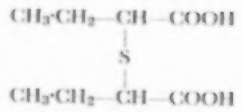
374 *rac.*-α-Thio-Di-n-buttersäure:



K_2 2,5·10⁻⁵	18	$\varkappa$ = 1,5 bis 2 $\mathcal{J}$ = 0,02 bis 0,2	**E3a** **D2**	unsicher.	L2

375 *meso*-α-Thio-Di-n-buttersäure:

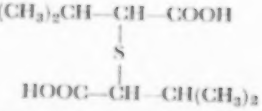


K_2 2,6·10⁻⁵	18	$\varkappa$ = 1,5 bis 2 $\mathcal{J}$ = 0,02 bis 0,2	**E3a** **D2**	unsicher.	L2

376 γ-Thio-Di-n-buttersäure: $COOH{\cdot}(CH_2)_3{\cdot}S{\cdot}(CH_2)_3{\cdot}COOH$

K_1 4,46·10⁻⁵ K_2 5,53·10⁻⁶	18	$\varkappa$ = 0,7 bis 2 $\mathcal{J}$ = 0,1	**E3b** **D3**	rel. zuv.	A7

377 *rac.*-α-Thio-Di-iso-valeriansäure:



K_2 1,6·10⁻⁵	18	$\varkappa$ = 1,5 bis 2 $\mathcal{J}$ = 0,03 bis 0,1	**E3a** **D2**	unsicher.	L2

No.	Name, Formel u. Dissoziations-Konstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
378	*meso*-α-Thio-Di-iso-valeriansäure: $(CH_3)_2CH{-}CH{-}COOH$ / S / $(CH_3)_2CH{-}CH{-}COOH$ (beide CH über S verbunden)					
	K_2 1,4·10⁻⁵	18	ϰ = 1,5 bis 2 ℑ = 0,03 bis 0,1	**E3a** **D2**	unsicher.	L2
379	10-(Aminoäthyl-thio)-n-Decansäure: $COOH{\cdot}(CH_2)_9{\cdot}S{\cdot}(CH_2)_2{\cdot}NH_2$					
	pK_1 4,0 pK_2 8,3		ℑ ≤ 0,1	**E3b** **D1**	unsicher.	C13
380	11-(Aminoäthyl-thio)-n-Undecansäure: $COOH{\cdot}(CH_2)_{10}{\cdot}S{\cdot}(CH_2)_2{\cdot}NH_2$					
	pK_1 2,6 pK_2 9,6		ℑ < 0,1	**E3b** **D1**	unsicher.	C13
381	11,11′-(Dithio-bis-äthylamin)-Di-n-undecansäure: $[COOH{\cdot}(CH_2)_{10}{\cdot}NH{\cdot}(CH_2)_2{\cdot}S{\cdot}]_2$					
	pK_1 3,2 pK_2 9,9		ℑ < 0,1	**E3b** **D1**	unsicher.	C13
382	α-Methylsulfonyl-Propionsäure: $CH_3{\cdot}SO_2{\cdot}CH(CH_3){\cdot}COOH$					
	3,6·10⁻³	25		**L2**	unsicher. Ohne nähere Angaben.	M16
383	α-Äthylsulfonyl-Propionsäure: $CH_3{\cdot}CH_2{\cdot}SO_2{\cdot}CH(CH_3){\cdot}COOH$					
	3,25·10⁻³	25		**L2**	unsicher. Ohne nähere Angaben.	M16

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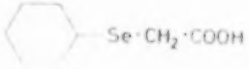
384 α-n-Propylsulfonyl-Propionsäure: $CH_3{\cdot}(CH_2)_2{\cdot}SO_2{\cdot}CH(CH_3){\cdot}COOH$

$3{,}11{\cdot}10^{-3}$	25		**L2**	unsicher. Ohne nähere Angaben.	M16

385 α-iso-Propylsulfonyl-Propionsäure: $(CH_3)_2CH{\cdot}SO_2{\cdot}CH(CH_3){\cdot}COOH$

$3{,}01{\cdot}10^{-3}$	25		**L2**	unsicher. Ohne nähere Angaben.	M16

386 Cyclohexyl-seleno-Essigsäure:



$6{,}50{\cdot}10^{-4}$	25		**L**	unsicher. Ohne nähere Angaben.	M28 M29

387 ε,ε,ε-Trifluor-Norleucin: $CF_3{\cdot}(CH_2)_3{\cdot}CH(NH_2){\cdot}COOH$

pK_1 2,164 pK_2 9,463	25	$\mathcal{J} = 0{,}03$	**E1a**	zuv.	W2

388 δ,δ,δ-Trifluor-Leucin: $CF_3{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$

pK_1 2,045 pK_2 8,942	25	$\mathcal{J} = 0{,}3$	**E1a**	zuv.	W2

389 δ,δ,δ-Trifluor-Norvalin: $CF_3{\cdot}(CH_2)_2{\cdot}CH(NH_2){\cdot}COOH$

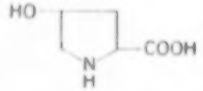
pK_1 2,042 pK_2 8,916	25	$\mathcal{J} = 0{,}03$	**E1a**	zuv.	W2

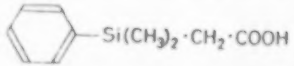
390 γ,γ,γ-Trifluor-Valin: $CF_3{\cdot}CH(CH_3){\cdot}CH(NH_2){\cdot}COOH$

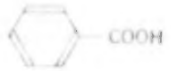
pK_1 1,537 pK_2 8,098	25	$\mathcal{J} = 0{,}03$	**E1a**	zuv.	W2

391 γ,γ,γ-Trifluor-α-Amino-n-Buttersäure: $CF_3{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$

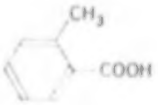
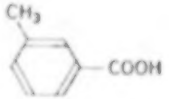
pK_1 1,600 pK_2 8,169	25	$\mathcal{J} = 0{,}03$	**E1a**	zuv.	W2

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
392	γ,γ,γ-Trifluor-Threonin: $CF_3{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 1,554 pK_2 7,822	25	$\mathcal{J} = 0{,}03$	**E1a**	zuv.	W2
393	γ,γ,γ-Trifluor-β-Amino-n-Buttersäure: $CF_3{\cdot}CH(NH_2){\cdot}CH_2{\cdot}COOH$					
	pK_1 2,756 pK_2 5,822	25	$\mathcal{J} = 0{,}03$	**E1a**	zuv.	W2
394	Serin: $CH_2(OH){\cdot}CH(NH_2){\cdot}COOH$					
	K_1 $6{,}22{\cdot}10^{-3}$ K_2 $7{,}08{\cdot}10^{-9}$	25		**E3b**	unsicher. Aktivitätskoeffizienten denjenigen der Essigsäure gleichgesetzt.	S10
395	Oxyprolin: 					
	K_1 $1{,}21{\cdot}10^{-2}$ K_2 $1{,}86{\cdot}10^{-10}$	25		**E3b**	unsicher. Aktivitätskoeffizienten denjenigen der Essigsäure gleichgesetzt.	S10
396	β-Oxy-Glutaminsäure: $COOH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}COOH$					
	K_1 $4{,}75{\cdot}10^{-3}$ K_2 $5{,}82{\cdot}10^{-5}$ K_3 $2{,}76{\cdot}10^{-10}$	25		**E3b**	unsicher. Aktivitätskoeffizienten denjenigen der Essigsäure gleichgesetzt.	S10

397	Canavanin: $NH_2{\cdot}C(NH_2){\cdot}NH{\cdot}O{\cdot}(CH_2)_2{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 2,50 pK_2 6,60 pK_3 9,25	25		**E3b**	unsicher.	T6
398	Canalin: $NH_2{\cdot}O{\cdot}(CH_2)_2{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 2,40 pK_2 3,70 pK_3 9,20	25		**E3b**	unsicher.	T6
399	Cystin: $[COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S{\cdot}]_2$					
	pK_1 < 1 pK_2 2,1 pK_3 8,02 pK_4 8,71	35	$c = 0{,}1$	**E3b**	unsicher.	G18
400	*S*-Äthyl-Cystein: $CH_3{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$					
	pK_1 2,03 pK_2 8,60		$J = 0{,}1$	**E3b**	unsicher.	R4
401	Organosiliciumsäuren: $(CH_3)_3{\cdot}Si{\cdot}(CH_2)_n{\cdot}COOH$					
	n = 1 $0{,}60{\cdot}10^{-5}$ n = 2 1,24 n = 3 1,30 n = 4 1,09 n = 5 0,87	25			unsicher. Ohne nähere Angaben.	S26
402	Pentamethyldisiloxanyl-Essigsäure: $(CH_3)_3Si{\cdot}O{\cdot}Si(CH_3)_2{\cdot}CH_2{\cdot}COOH$					
	$0{,}60{\cdot}10^{-5}$	25		**E**	unsicher. Ohne nähere Angaben.	S25
403	Dimethyl-Phenyl-silyl-Essigsäure: 					
	$0{,}54{\cdot}10^{-5}$	25		**E**	unsicher. Ohne nähere Angaben	S25

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
404	Benzoesäure 					
	(*m*) $6{,}25 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}003$ bis $0{,}001$	**E3c** **R2c**	rel. zuv. Mit Zelle ohne Diffusionspotentiale. Glaselektrode. Unsicheres Rechenverfahren. Unsicherheiten in Bestimmung der Neigung der Titrationskurve.	G23
	(*c*) $6{,}527 \cdot 10^{-5}$	25	$c = 0{,}002$ bis $0{,}0002$	**L1** u. **L2** abnl. **R1a** abnl. **R1e** **K1d**	rel. zuv. Apparative Mängel (Glaszellen, Parkereffekt, Wasserthermostat, falsche Erdung (vgl. I4))	I2
	(*c*) $6{,}27 \cdot 10^{-5}$	25	$\varkappa = 0{,}8$ bis $1{,}1$ $c = 0{,}0005$ bis $0{,}008$	**L1** **R1a** **K2e**	rel. zuv. Apparative Mängel (Glaszellen, Parkereffekt, Wasserthermostat). Unsichere Solvenskorr. Keine Angaben über Hydrolysekorr.	D18
	(*c*) $6{,}138 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}003$ bis $0{,}03$	**O2**	rel. zuv. Relative Konstante gegen Bromphenolblau bestimmt; für letzteres nicht direkt gemessen, sondern schrittweise aus dem Konstantenverhältnis mehrerer anderer Säuren ermittelt. Keine Korr. für Reaktion der Puffermischung mit H_2O und dem zugesetzten Indikator.	M21
	(*m*) $6{,}15 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}017$ bis $0{,}08$	**E1a**	rel. zuv. Wie bei Phenol (A1).	A1

(*m*) 6,237·10⁻⁵ 6,295 6,266 6,237	20 25 30 35	$\mathcal{I}$ = 0,01 bis 0,04	**E1a**	rel. zuv. E.M.K.-Werte waren zeitabhängig. Für E_0 ein Wert verwendet (H21), der ebenfalls aus zeitabhängigen E.M.K.-Werten gewonnen wurde.	J9
(*c*) 6,373·10⁻⁵	25	$\varkappa$ = 0,7 bis 0,8 c = 0,0001 bis 0,01	**L1** **K1c** **R1b**	rel. zuv. bis zuv. Apparative Mängel (Parkereffekt). Verwendung empirischer "n-Formeln" statt Onsager-gleichung.	J6
(*c*) 6,312·10⁻⁵(1) 6,320·10⁻⁵(2)	25	$\varkappa$ = 0,16 $\mathcal{I}$ = 0,0003	**L1** **R1a** **K1a**	s. zuv. Die Werte (1) und (2) wurden mit verschiedenen Werten für $\varkappa_{KCl}$ (zur Bestimmung der Zellkonstanten) berechnet. Der zweite Wert ist der mit neueren Daten berechnete.	B53
(*c*) 6,295·10⁻⁵	25	$\varkappa$ = 0,1 $\mathcal{I}$ = 0,001 bis 0,02	**L1** **R1b** **K2a**	zuv. Hydrolysekorr. etwas unsicher (vgl. J6) Ionenstärken relativ hoch.	S7
(*m*) 6,11·10⁻⁵ 6,13 6,12 6,09 6,01 5,86 5,74	15 20 25 30 35 40 45	$\mathcal{I}$ = 0,009 bis 0,02	**E1a**	rel. zuv. Zur Bestimmung der E_0-Werte wird die Konstante A in der D.–H.-Gl. T-unabhängig zu 0,5 angenommen. Deshalb sind wahrscheinlich alle Werte bei $T \neq 15$°C etwas falsch.	B49
(*m*) 6,7·10⁻⁵	25	$\mathcal{I}$ = 0,003 bis 0,05	**E3a** **D1**	rel. zuv. bis unsicher. Diffusionspotentiale. Keine Angaben über Hydrolysekorr.	K30
(*m*) 6,05·10⁻⁵	25	$\mathcal{I}$ = 0,02 bis 0,08	**E1a**	rel. zuv. Mit Wasserstoffelektrode. Etwas inkonstante Potentiale. (Vgl. Kritik bei (J9))	B50
(*c*) 6,09·10⁻⁵	18	$\mathcal{I}$ = 0,01 bis 0,02	**E2b**	zuv.	L11
(*m*) 6.32·10⁻⁵	25	$\mathcal{I}$ = 0,1	**E2c**	rel. zuv. Bezugssäure Cyclohexancarbonsäure. Über die Sicherheit des -Wertes für diese vgl. dort (K8).	K10
				Weitere Messungen: A14; B32; B33; B44; B55; F3; H7; H11; H23; I3; J14; K25; K29; L3; L6; L14; M13; R3; S18.	

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
405	*o*-Tolylsäure: 					
	$1{,}235 \cdot 10^{-4}$	25	$\varkappa = 1$ $c = 0{,}0005$ bis $0{,}003$	**L1** **R1a** **K2e**	rel. zuv.	D14
					Weitere Messung: R3.	
406	*m*-Tolylsäure: 					
	$5{,}35 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0008$ bis $0{,}0025$	**L1** **R1a** **K2e**	rel. zuv.	D15
					Weitere Messung: (nur Wert zitiert) B49.	
407	*p*-Tolylsäure:					
	$4{,}24 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0008$ bis $0{,}0015$	**L1** **R1a** **K2e**	rel. zuv.	D15
					Weitere Messung: (nur Wert zitiert) B49.	

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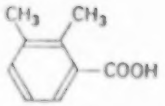
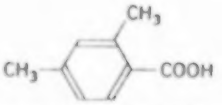
408 2,3-Dimethyl-Benzoesäure:



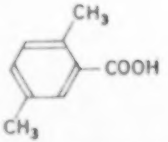
$1{,}83 \cdot 10^{-4}$	25	$\varkappa = 0{,}7$ bis $0{,}9$ $c = 0{,}002$ bis $0{,}0003$	**L1** **R1a** **K2e** **K1a**	rel. zuv. Glaszellen, Wasserthermostat, unsichere Solvens- u. Hydrolysekorr.	D12

409 2,4-Dimethyl-Benzoesäure:

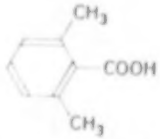
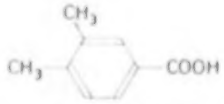
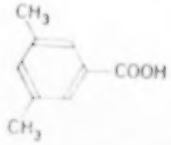


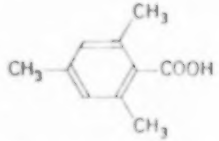
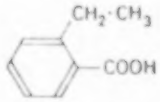
$6{,}57 \cdot 10^{-5}$	25	$\varkappa = 0{,}7$ bis $0{,}9$ $c = 0{,}001$ bis $0{,}0003$	**L1** **R1a** **K2e** **K1a**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure.	D12

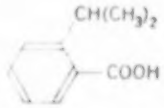
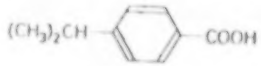
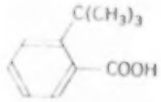
410 2,5-Dimethyl-Benzoesäure:

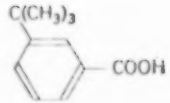
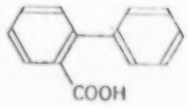


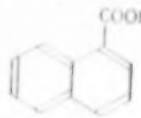
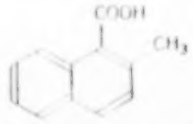
$1{,}055 \cdot 10^{-4}$	25	$\varkappa = 0{,}7$ bis $0{,}9$ $c = 0{,}0002$ bis $0{,}001$	**L1** **R1a** **K2e** **K1a**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure.	D12

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
411	2,6-Dimethyl-Benzoesäure: 					
	$5{,}68 \cdot 10^{-4}$	25	$\varkappa = 0{,}7$ bis $0{,}9$ $c = 0{,}0003$ bis $0{,}001$	**L1** **R1a** **K2e** **K1a**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure.	D12
412	3,4-Dimethyl-Benzoesäure: 					
	$3{,}91 \cdot 10^{-5}$	25	$\varkappa = 0{,}7$ bis $0{,}9$ $c = 0{,}0002$ bis $0{,}0007$	**L1** **R1a** **K2e** **K1a**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure.	D12
413	3,5-Dimethyl-Benzoesäure: 					

	$5{,}00 \cdot 10^{-5}$	25	$\varkappa = 0{,}7$ bis $0{,}9$ $c = 0{,}0002$ bis $0{,}0006$	**L1** **R1a** **K2e** **K1a**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure.	D12
414	2,4,6-Trimethyl-Benzoesäure: 					
	$3{,}66 \cdot 10^{-4}$	25	$\varkappa = 0{,}7$ bis $0{,}9$ $c = 0{,}0002$ bis $0{,}001$	**L1** **R1a** **K2c** **K1a**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure.	D12
	pK 3,43	25	$\mathcal{J} = 0{,}03$ bis $0{,}111$	**O2**	rel. zuv.	C27
415	*o*-Äthyl-Benzoesäure: 					
	$1{,}61 \cdot 10^{-4}$	25	$\varkappa = 0{,}7$ $c = 0{,}00008$ bis $0{,}0007$	**L1** **R1a** **K1a** **K2e**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure.	D12
416	*p*-Äthyl-Benzoesäure:					
	$4{,}435 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0003$ bis $0{,}001$	**L1** **R1a** **K2e**	rel. zuv. Apparative Mängel: Zellen, Parkereffekt, Wasserthermostat, unsichere Solvenskorr. Keine Angaben über Hydrolysekorr.	B6

No.	*Name, Formel u. Dissoziationskonstante k*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
417	*o*-iso-Propyl-Benzoesäure: 					
	$2{,}315 \cdot 10^{-4}$	25	$\varkappa = 0{,}7$ $c = 0{,}0002$ bis $0{,}0007$	**L1** **R1a** **K1a** **K2e**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure (D12).	**D12**
418	*p*-iso-Propyl-Benzoesäure: 					
	$4{,}43 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0002$ bis $0{,}0004$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *p*-Äthyl-Benzoesäure.	**B6**
419	*o*-tert.-Butyl-Benzoesäure: 					
	$2{,}91 \cdot 10^{-4}$	25	$\varkappa = 0{,}7$ bis $0{,}9$ $c = 0{,}0003$ bis $0{,}001$	**L1** **R1a** **K1a** **K2e**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure.	**D12**

	$3{,}5 \cdot 10^{-4}$	25	$c > 0{,}0003$	**L2**	unsicher. Λ_0 der Säure aus der Zahl der Atome im Molekül abgeschätzt.	S18
420	*m*-tert.-Butyl-Benzoesäure: 					
	K_c $5{,}2 \cdot 10^{-5}$	25	$c > 0{,}0003$	**L2**	unsicher. Wie bei *o*-tert.-Butyl-Benzoesäure (S18).	S18
421	*p*-tert.-Butyl-Benzoesäure:					
	$3{,}98 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0002$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *p*-Äthyl-Benzoesäure.	B6
					Weitere Messungen: S18.	
422	*o*-Phenyl-Benzoesäure: 					
	$3{,}47 \cdot 10^{-4}$	fehlt	$\varkappa = 0{,}9$ bis 1 $c = 0{,}00008$ bis $0{,}0004$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *o*-Tolylsäure (D14).	D14

No.	Name, Formel u. Dissoziationskonstante k	T (°C)	Bemerkungen	Methode	Kritik	Lit.
423	Naphthoesäure-1: 					
	$2{,}03 \cdot 10^{-4}$	20	$\varkappa = 1$ $c = 0{,}001$	**E3b**	unsicher. A_z-Werte. Keine exper. Angaben.	L14
	$2{,}02 \cdot 10^{-4}$	25	$\varkappa \geq 0{,}7$ $c = 0{,}00009$ bis $0{,}0002$	**L1** **R1a** **K1a** **K2e**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure (D12).	D12
424	Naphthoesäure-2:					
	$6{,}30 \cdot 10^{-5}$	20	$\varkappa = 1$ $c = 0{,}001$	**E3b**	unsicher. A_z-Werte. Keine exper. Angaben.	L14
	$6{,}30 \cdot 10^{-5}$	25	$\varkappa = 0{,}7$ $c = 0{,}0001$ bis $0{,}0002$	**L1** **R1a** **K1a** **K2e**	rel. zuv. Wie bei 2,3-Dimethyl-Benzoesäure (D12).	D12
425	2-Methyl-Naphthoesäure-1: 					
	k $7{,}8 \cdot 10^{-4}$	25	$J = 0{,}03$ bis $0{,}111$	**O2**	rel. zuv.	C27

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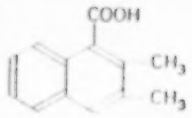
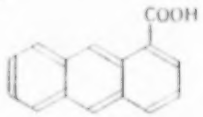
426 2,3-Dimethyl-Naphthoesäure-1:



$4{,}7 \cdot 10^{-4}$	25	$f = 0{,}03$ bis $0{,}076$	**O2**	rel. zuv.	627

427 Anthracen-carbonsäure-1:

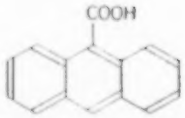


$2{,}076 \cdot 10^{-4}$	20	$\varkappa = 1$ $c = 0{,}001$	**E3b**	unsicher. K_c-Werte. Keine exper. Angaben.	L14

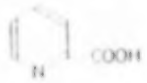
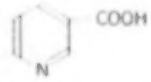
428 Anthracen-carbonsäure-2:

$6{,}65 \cdot 10^{-5}$	20	$\varkappa = 1$ $c = 0{,}001$	**E3b**	unsicher. K_c-Werte. Keine exper. Angaben.	L14

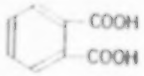
429 Anthracen-carbonsäure-9:



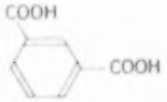
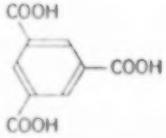
$2{,}215 \cdot 10^{-4}$	20	$\varkappa = 1$ $c = 0{,}001$	**E3b**	unsicher. K_c-Werte. Keine exper. Angaben.	L14

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
430	Picolinsäure: 					
	K_1 0,403·10^{-5} K_2 0,102·10^{-12}	25	$\mathcal{J} = 0{,}03$	**O5**	rel. zuv. Extrapol. mit $\log f_i = A\sqrt{\mathcal{J}}/(1+\sqrt{\mathcal{J}})$.	E9
431	Nicotinsäure: 					
	K_1 1,50·10^{-5} K_2 1,04·10^{-12}	25	$\mathcal{J} = 0{,}03$	**O5**	rel. zuv. Extrapol. mit $\log f_i = A\sqrt{\mathcal{J}}/(1+\sqrt{\mathcal{J}})$.	E9
	K_1 1,18·10^{-5} K_2 3,55·10^{-11}	22	$\mathcal{J} = 0{,}01$	**O5**	unsicher. Photographisch.	H39
432	Isonicotinsäure:					
	K_1 1,46·10^{-5} K_2 0,59·10^{-12}	25	$\mathcal{J} = 0{,}015$	**O5**	rel. zuv. Extrapol. mit $\log f_i = A\sqrt{\mathcal{J}}/(1+\sqrt{\mathcal{J}})$.	E9

433 Phthalsäure:



(*m*)	K_1 1,190·10⁻³	0	$\varkappa = 0{,}6$ bis 1	**E1a**	sehr zuv.	H9
	K_2 3,696·10⁻⁶		$\mathcal{J} = 0{,}002$ bis 0,04			H10
	K_1 1,182·10⁻³	5				
	K_2 3,820·10⁻⁶					
	K_1 1,171·10⁻³	10				
	K_2 3,894·10⁻⁶					
	K_1 1,157·10⁻³	15				
	K_2 3,934·10⁻⁶					
	K_1 1,141·10⁻³	20				
	K_2 3,937·10⁻⁶					
	K_1 1,123·10⁻³	25				
	K_2 3,906·10⁻⁶					
	K_1 1,102·10⁻³	30				
	K_2 3,840·10⁻⁶					
	K_1 1,078·10⁻³	35				
	K_2 3,740·10⁻⁶					
	K_1 1,053·10⁻³	40				
	K_2 3,611·10⁻⁶					
	K_1 1,027·10⁻³	45				
	K_2 3,454·10⁻⁶					
	K_1 0,998·10⁻³	50				
	K_2 3,274·10⁻⁶					
	K_1 0,968·10⁻³	55				
	K_2 3,075·10⁻⁶					
	K_1 0,937·10⁻³	60				
	K_2 2,875·10⁻⁶					
	K_1 1,01·10⁻³	50	$\mathcal{J} = 0{,}025$ bis 1	**E3b**	rel. zuv.	O4
				D2		
	K_2 4,0·10⁻⁶	18	$\varkappa = 1{,}5$ bis 2	**E3a**	unsicher.	L2
			$\mathcal{J} = 0{,}011$ bis 0,3	**D2**	$\log f_\pm = A\sqrt{\mathcal{J}}$.	
	K_2 4,65·10⁻⁶	30	$\mathcal{J} = 0{,}086$ bis 0,5	**E3a**	unsicher.	M27
				D1	Wenig Angaben.	
					Weitere Messungen: B12; H2; L2; M13; M15.	

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
434	Isophthalsäure: 					
	K_1 2,4·10^{-4}	25	$\mathcal{I} = 0{,}03$	**O5**	unsicher.	T3
	K_2 2,5·10^{-5}				Sehr kleine Differenz zwischen K_1 und K_2.	
					Weitere Messungen: M13; M14; M15.	
435	Terephthalsäure:					
	K_1 2,9·10^{-4}	25	$\mathcal{I} = 0{,}03$	**O5**	unsicher.	T3
	K_2 3,5·10^{-5}					
	K_2 1,59·10^{-5}	16	$\varkappa = 3$	**E3a**	unsicher.	K40
			$\mathcal{I} = 0{,}12$	**D1**	$\log f_\pm = A\sqrt{\mathcal{I}}$.	
436	Benzol-1,3,5-tricarbonsäure (Trimesinsäure): 					
	K_1 7,5·10^{-3}		$\mathcal{I} = 0{,}03$	**E3b**	unsicher.	M14
	K_2 1,28·10^{-4}				K_n-Werte.	M15
	K_3 2,0·10^{-5}					

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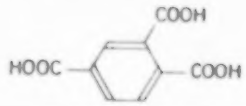
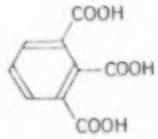
437 Benzol-1,2,4-tricarbonsäure (Trimellithsäure):



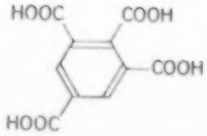
K_1 $3{,}0 \cdot 10^{-3}$ K_2 $1{,}45 \cdot 10^{-4}$ K_3 $6{,}3 \cdot 10^{-6}$	$\mathcal{I} = 0{,}03$	**E3b**	unsicher. K_c-Werte.	M14 M15

438 Benzol-1,2,3-tricarbonsäure (Hemimellithsäure):

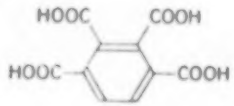
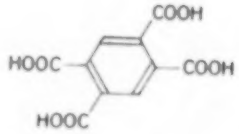
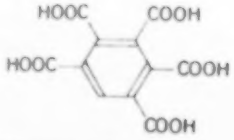


K_1 $1{,}60 \cdot 10^{-3}$ K_2 $6{,}3 \cdot 10^{-5}$ K_3 $1{,}35 \cdot 10^{-6}$	$\mathcal{I} = 0{,}03$	**E3b**	unsicher. K_c-Werte.	M14 M15

439 Benzol-1,2,3,5-tetracarbonsäure (Prehnitsäure):



K_1 $4{,}2 \cdot 10^{-3}$ K_2 $3{,}1 \cdot 10^{-4}$ K_3 $3{,}6 \cdot 10^{-5}$ K_4 $1{,}55 \cdot 10^{-6}$	$\mathcal{I} = 0{,}03$	**E3b**	unsicher. K_c-Werte.	M14 M15

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
440	Benzol-1,2,3,4-tetracarbonsäure (Mellophansäure): 					
	K_1 8,8·10^{-3} K_2 5,6·10^{-4} K_3 1,87·10^{-5} K_4 6,1·10^{-7}		$\mathcal{I} = 0{,}03$	**E3b**	unsicher. K_c-Werte.	M14 M15
441	Benzol-1,2,4,5-tetracarbonsäure (Pyromellithsäure): 					
	K_1 1,20·10^{-2} K_2 1,34·10^{-3} K_3 3,2·10^{-5} K_4 2,35·10^{-6}		$\mathcal{I} = 0{,}03$	**E3b**	unsicher. K_c-Werte.	M14 M15
442	Benzol-pentacarbonsäure: 					

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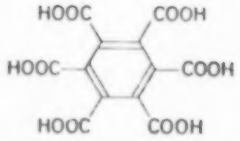
K_1 1,60·10^{-2} K_2 1,85·10^{-3} K_3 1,08·10^{-4} K_4 5,6·10^{-6} K_5 3,5·10^{-7}	$\mathcal{J} = 0{,}03$	**E3b**	unsicher. K_c-Werte.	M13

443 Benzol-hexacarbonsäure (Mellithsäure):



K_1 4,0·10^{-2} K_2 6,4·10^{-3} K_3 4,9·10^{-4} K_4 1,65·10^{-5} K_5 1,28·10^{-6} K_6 1,10·10^{-7}	$\mathcal{J} = 0{,}03$	**E3b**	unsicher. K_c-Werte.	M13

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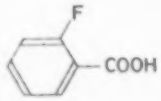
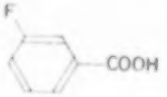
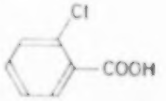
444 *o*-Fluor-Benzoesäure:

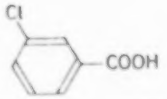


5,41·10^{-4}	25	$\varkappa = 1$ $c = 0{,}0008$ bis $0{,}004$	**L1** **R1a** **K2e**	rel. zuv. Wie *p*-Tolylsäure (D15).	D15
1,26·10^{-3}	17	$\varkappa = 1$ $\mathcal{J} = 0{,}12$	**E3a** **D1**	unsicher. $\log f_\pm = A\sqrt{\mathcal{J}}$.	K39

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
445	*m*-Fluor-Benzoesäure: 					
	$1{,}365 \cdot 10^{-4}$	25	$\varkappa = 1$ $c = 0{,}0006$ bis $0{,}0036$	**L1** **R1a** **K2e**	rel. zuv. Wie *p*-Tolylsäure (D15).	D15
	$1{,}41 \cdot 10^{-4}$	16	$\varkappa = 3$ $\bar{f} = 0{,}12$	**E3a** **D1**	unsicher. $\log f_i = A\sqrt{I}$.	K39
446	*p*-Fluor-Benzoesäure:					
	$7{,}22 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0002$ bis $0{,}004$	**L1** **R1a** **K2e**	rel. zuv.	D19
	$9{,}12 \cdot 10^{-5}$	15	$\varkappa = 3$ $\bar{f} = 0{,}12$	**E3a** **D1**	unsicher. $\log f_i = A\sqrt{I}$.	K39
447	*o*-Chlor-Benzoesäure: 					

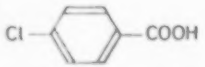
1,198·10⁻³	25	$\varkappa = 0{,}1$ $\mathcal{J} = 0{,}0002$ bis $0{,}01$	**L1** **R1b** **K2a**	zuv.	S7
1,233·10⁻³	25	$\varkappa = 1$ $c = 0{,}0008$ bis $0{,}007$	**L1** **R1b**	rel. zuv. Wie bei Ameisensäure (D1).	D1
1,14·10⁻³	25	$\varkappa = 1$ $\mathcal{J} = 0{,}0004$ bis $0{,}003$	**L1** **R1a** **K2e**	rel. zuv.	D19
1,215·10⁻³	25	$\varkappa = 1$ $c = 0{,}0004$ bis $0{,}006$	**L1** **R1b**	unsicher.	M3
(*m*) 1,23·10⁻³ (a) 1,24·10⁻³ (b)	20	$\varkappa = 0{,}6$ $\mathcal{J} = 0{,}01$	**O4**	rel. zuv. (a) und (b) mit verschiedenen Indikatoren.	K34
				Weitere Messungen: B28; B55.	

448 *m*-Chlor-Benzoesäure:



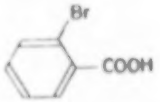
1,507·10⁻⁴	25	$c = 0{,}0002$ bis $0{,}011$	**L1** **R1b** **K2a**	zuv.	S7
1,48·10⁻⁴	25	$\varkappa = 1$ $c = 0{,}0002$ bis $0{,}001$	**L1** **R1a** **K2e**	rel. zuv.	D19

449 *p*-Chlor-Benzoesäure:



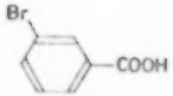
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*		*Kritik*	*Lit.*
	(*m*) $1{,}00 \cdot 10^{-3}$	15	$\mathcal{J} = 0{,}007$ bis $0{,}01$	**E1a**	sehr zuv.		B49
	$1{,}02$	20					
	$1{,}032$	25					
	$1{,}045$	30					
	$1{,}045$	35					
	$1{,}045$	40					
	$1{,}035$	45					
	$1{,}04 \cdot 10^{-3}$	25	$\varkappa = 0{,}1$ $\mathcal{J} = 0{,}0002$ bis $0{,}01$	**L1** **R1b** **K2a**	rel. zuv.		S7
	$1{,}055 \cdot 10^{-3}$	25	$\varkappa = 1$ $c = 0{,}0001$ bis $0{,}0004$	**L1** **R1a** **K2c**	rel. zuv.		D19

450 *o*-Brom-Benzoesäure:



	$1{,}40 \cdot 10^{-3}$	25	$\varkappa = 1$ $c = 0{,}0007$ bis $0{,}005$	**L1** **R1a** **K2c**	rel. zuv.		D19

451 *m*-Brom-Benzoesäure:

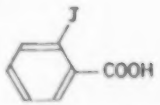


(*m*) $1{,}516 \cdot 10^{-3}$	15	$\mathcal{J} = 0{,}008$ bis $0{,}01$	**E1a**	sehr zuv.	B49
1,537	20				
1,553	25				
1,55	30				
1,55	35				
1,538	40				
1,52	45				
$1{,}54 \cdot 10^{-3}$	25	$\varkappa = 1$ $c = 0{,}0004$ bis $0{,}0013$	**L1** **R1a** **K2e**	rel. zuv.	D15
				Weitere Messung: B55.	

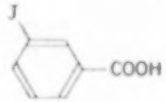
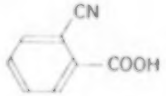
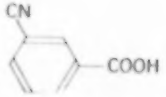
452 *p*-Brom-Benzoesäure:

$1{,}07 \cdot 10^{-4}$	25	$\varkappa = 1$ $\mathcal{J} = 0{,}0001$ bis $0{,}0002$	**L1** **R1a** **K2e**	rel. zuv.	D19
(*m*) $9{,}73 \cdot 10^{-5}$	15	$\mathcal{J} = 0{,}007$ bis $0{,}01$	**E1a**	sehr zuv.	B49
9,88	20				
$9{,}95_4$	25				
9,95	30				
9,97	35				
$9{,}88_6$	40				
9,84	45				

453 *o*-Jod-Benzoesäure:



$1{,}37 \cdot 10^{-3}$	25	$\varkappa = 1$ $c = 0{,}0004$ bis $0{,}0023$	**L1** **R1a** **K2e**	rel. zuv.	D15

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
454	*m*-Jod-Benzoesäure: 					
	$1{,}41 \cdot 10^{-4}$	25	$\varkappa = 1$ $\epsilon = 0{,}00008$ bis $0{,}00036$	**L1** **R1a** **K2e**	rel. zuv.	D15
	$1{,}39 \cdot 10^{-4}$	25			Wert zitiert.	B49
455	*o*-Cyan-Benzoesäure: 					
	K_c $7{,}29 \cdot 10^{-4}$	25		**L2**	unsicher. Rasche Hydrolyse	W8
456	*m*-Cyan-Benzoesäure: 					
	(*m*) $2{,}463 \cdot 10^{-4}$	15	$\mathcal{J} = 0{,}007$ bis $0{,}01$	**E1a**	sehr zuv.	B49
	$2{,}518$	20				
	$2{,}526$	25				
	$2{,}533$	30				

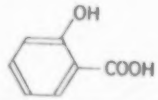
	2,516	35				
	2,48	40				
	2,44	45				
	$2{,}092 \cdot 10^{-4}$	25	$\mathcal{I} = 0{,}05$	**E2c**	rel. zuv.	K6
	K_c $2{,}5 \cdot 10^{-4}$	25		**L2**	unsicher. Rasche Hydrolyse.	W8

457 *p*-Cyan-Benzoesäure:

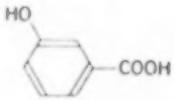
	(*m*) $2{,}77 \cdot 10^{-4}$	15	$\mathcal{I} = 0{,}008$ bis 0,01	**E1a**	sehr zuv.	B49
	$2{,}812$	20				
	$2{,}812$	25				
	$2{,}879$	30				
	$2{,}795$	35				
	$2{,}748$	40				
	$2{,}712$	45				
	$2{,}831 \cdot 10^{-4}$	25	$\mathcal{I} = 0{,}05$	**E2c**	rel. zuv.	K6
	$3{,}10 \cdot 10^{-4}$	25		**E2b**	unsicher.	K25

213

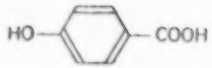
458 Salizylsäure:



	K_1 $1{,}76 \cdot 10^{-3}$ K_2 $4{,}20 \cdot 10^{-13}$	30	$\mathcal{I} = 0{,}003$ bis 0,013	**E3b** **D1**	unsicher. Keine Angaben über Hydrolysekorr.	A2
	K_1 $1{,}25 \cdot 10^{-3}$	30	$\mathcal{I} = 0{,}008$ bis 0,05	**E1a**	rel. zuv. Für Korrekturgrößen wurden auch Messungen mit Ketten mit Diffusionspotentialen herangezogen.	A3

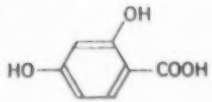
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	K_1 1,07·10⁻³	19	$\varkappa = 3$ $\mathcal{J} = 0{,}008$ bis $0{,}14$	**E3a** **D1**	unsicher. $\log f_\pm = A\sqrt{\mathcal{J}}$.	K38
	K_1 9,4·10⁻⁴	18	$\mathcal{J} = 0{,}006$ bis 2	**E2b**	zuv.	L11
	K_1 1,05$_2$·10⁻³	25	$\mathcal{J} = 0{,}003$ bis $0{,}03$	**O2**	rel. zuv. Indikator: Dinitro-Phenol, geeicht mit Benzoesäure (B53).	M21
	K_2 4·10⁻¹¹	Zim. temp.	$\mathcal{J} = 0{,}03$ bis $0{,}06$	**O3**	unsicher. Mit mehreren Indikatoren.	K32
	K_2 4·10⁻¹¹	18	$\mathcal{J} = 0{,}02$ bis $0{,}06$	**E3a** **D2**	unsicher. $\log f_\pm = A\sqrt{\mathcal{J}}$.	L5
					Weitere Messungen: B32; B33; B45; H7; H38; L1; R3.	
459	*m*-Oxy-Benzoesäure: 					
	K_1 8,33·10⁻⁵	25			zitiert.	B49
	K_1 6,96·10⁻⁵	18	$\mathcal{J} = 0{,}01$ bis $0{,}03$	**E2b**	zuv.	L11
	K_1 1,25·10⁻⁴ K_2 1,65·10⁻¹⁰	30	$\mathcal{J} = 0{,}001$ bis $0{,}018$	**E3b** **D1**	unsicher. Keine Angaben über Hydrolysekorr.	A2
	K_1 8,71·10⁻⁵ K_2 1,18·10⁻¹⁰	19	$\varkappa = 3$ $\mathcal{J} = 0{,}02$ bis $0{,}14$	**E3a** **D1**	unsicher. $\log f_\pm = A\sqrt{\mathcal{J}}$.	K38
	K_2 1,0·10⁻¹⁰	18	$\mathcal{J} = 0{,}02$ bis $0{,}06$	**E3a** **D2**	unsicher. $\log f_\pm = A\sqrt{\mathcal{J}}$.	L5

460 *p*-Oxy-Benzoesäure:



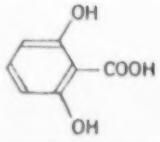
(*m*) K_1 2,53·10^{-5} 2,60 2,62 2,65$_5$ 2,64$_7$ 2,63 2,61	15 20 25 30 35 40 45	$\mathcal{J}$ = 0,009 bis 0,015	**E1a**	sehr zuv.	B49
pK_1 4,61 pK_2 9,31	27–28	$\mathcal{J}$ = 0,03 bis 0,061	**O2**	rel. zuv.	M11
K_1 5,15·10^{-5} K_2 7,46·10^{-10}	30	$\mathcal{J}$ = 0,001 bis 0,017	**E3b** **D1**	unsicher.	A2
K_1 7,46·10^{-5} K_2 4,79·10^{-10}	19	$\varkappa$ = 3 $\mathcal{J}$ = 0,02 bis 0,14	**E3a** **D1**	unsicher. $\log f_\pm = A\sqrt{\mathcal{J}}\mathcal{J}$.	L5

461 *β*-Resorzylsäure (2,4-Dioxy-Benzoesäure):

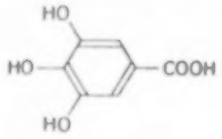
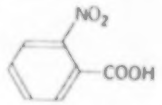
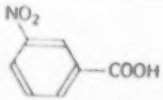


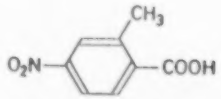
(*m*) K_1 6,05·10^{-4}	30	$\mathcal{J}$ = 0,01 bis 0,05	**E1a**	zuv.	A5

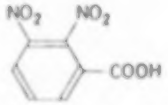
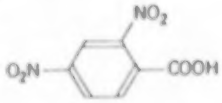
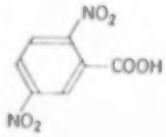
462 *γ*-Resorzylsäure (2,6-Dioxy-Benzoesäure):



6,00·10^{-2}	30	$\mathcal{J}$ = 0,02 bis 0,09	**E1a**	rel. zuv. Korrekturgrößen für m_H' wurden mit Ketten mit Diffusionspotential gemessen.	A3

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
463	Gallussäure (3,4,5-Trioxy-Benzoesäure): 					
	K_1 $4{,}63 \cdot 10^{-5}$ K_2 $1{,}41 \cdot 10^{-9}$	30	$\mathcal{I} = 0{,}0008$ bis $0{,}011$	**E3b** **D1**	unsicher.	A2
			214			
464	*o*-Nitro-Benzoesäure: 					
	$6{,}10 \cdot 10^{-3}$	25	$c = 0{,}001$ bis $0{,}03$	**L1** **R1b**	rel. zuv. Wie bei Ameisensäure (D1).	D1
	$6{,}71 \cdot 10^{-3}$	25	$\varkappa = 1$ $c = 0{,}001$ bis $0{,}02$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *o*-Tolylsäure (D14).	D14
	$5{,}99_5 \cdot 10^{-3}$	25	$\varkappa = 1$ $c = 0{,}001$ bis $0{,}003$	**L1** **R1b**	rel. zuv.	M3
					Weitere Messung: R3.	
465	*m*-Nitro-Benzoesäure: 					

	$3{,}55 \cdot 10^{-4}$	25			zitiert.	B49
	$3{,}21 \cdot 10^{-4}$	25	$\varkappa = 1$ $c = 0{,}005$ bis $0{,}003$	**L1** **R1** **K2e**	rel. zuv. Wie bei *p*-Tolylsäure (D15).	D15
466	*p*-Nitro-Benzoesäure:					
	(*m*) $3{,}556 \cdot 10^{-4}$ $3{,}60$ $3{,}61$ $3{,}63$ $3{,}60$ $3{,}59$ $3{,}547$	15 20 25 30 35 40 45	$\mathcal{J} = 0{,}007$ bis $0{,}009$	**E1a**	sehr zuv.	B49
	$3{,}55 \cdot 10^{-4}$	50	$c = 0{,}0007$ bis $0{,}0017$	**E3b**	unsicher. Wenig exper. Angaben.	B44
	$3{,}76 \cdot 10^{-4}$	25	$\varkappa = 1$ $c = 0{,}0005$ bis $0{,}0016$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *p*-Tolylsäure (D15).	D15
467	4-Nitro-*o*-Tolylsäure: 					
	$1{,}37 \cdot 10^{-2}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}00015$ bis $0{,}0008$	**L1** **R1a** **K2e**	unsicher.	D16

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
468	2,3-Dinitro-Benzoesäure: 					
	$1{,}41 \cdot 10^{-2}$	25	$\epsilon \simeq 10^{-4}$	**L2** **R1c**	rel. zuv. Apparat. Mängel; Zellen; Wasserthermostat; Parkereffekt.	D10
469	2,4-Dinitro-Benzoesäure: 					
	$3{,}76 \cdot 10^{-2}$	25	$\epsilon \simeq 10^{-4}$	**L2** **R1c**	rel. zuv. Apparat. Mängel; Zellen; Wasserthermostat; Parkereffekt.	D10
470	2,5-Dinitro-Benzoesäure: 					
	$2{,}39 \cdot 10^{-2}$	25	$\epsilon \simeq 10^{-4}$	**L2** **R1c**	rel. zuv. Apparat. Mängel; Zellen; Wasserthermostat; Parkereffekt.	D10

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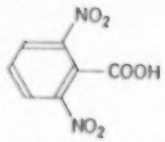
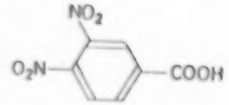
471 2,6-Dinitro-Benzoesäure:



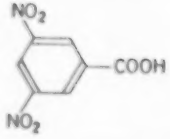
$7{,}25 \cdot 10^{-2}$	25	$\varepsilon \simeq 10^{-4}$	**L2** **R1c**	rel. zuv. Apparat. Mängel; Zellen; Wasserthermostat; Parker-effekt.	D10

472 3,4-Dinitro-Benzoesäure:

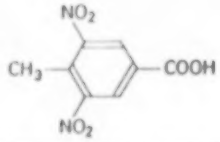
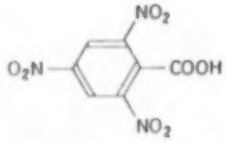
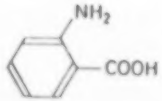


$1{,}52 \cdot 10^{-3}$	25	$\varepsilon \simeq 10^{-4}$	**L2** **R1c**	rel. zuv. Apparat. Mängel; Zellen; Wasserthermostat; Parker-effekt.	D10

473 3,5-Dinitro-Benzoesäure:



$1{,}51 \cdot 10^{-3}$	25	$\varepsilon = 0{,}0005$ bis $0{,}004$	**L1** **R1b**	rel. zuv. Wie bei Ameisensäure (D1). Wenig Meßpunkte.	D1
$1{,}505 \cdot 10^{-3}$	25	$\varkappa = 1$ $\varepsilon = 0{,}0005$ bis $0{,}004$	**L1** **R1b**	rel. zuv.	M3
$1{,}50 \cdot 10^{-3}$	25	$\varepsilon \simeq 10^{-4}$	**L2** **R1c**	rel. zuv. Siehe 2,3-Dinitro-Benzoesäure (D10).	D10
				Weitere Messung von K_ε siehe H38.	

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
474	3,5-Dinitro-*p*-Tolylsäure: 					
	$1{,}07 \cdot 10^{-3}$	25	$c \simeq 10^{-4}$	**L2** **R1c**	rel. zuv. Siehe 2,3-Dinitro-Benzoesäure (D10).	D10
475	2,4,6-Trinitro-Benzoesäure: 					
	$2{,}22 \cdot 10^{-1}$	25	$c \simeq 10^{-4}$	**L2** **R1c**	rel. zuv. Siehe 2,3-Dinitro-Benzoesäure (D10).	D10
			215			
476	*o*-Amino-Benzoesäure (Anthranilsäure): 					

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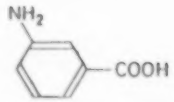
K_1 $7{,}32 \cdot 10^{-3}$ K_2 $1{,}60 \cdot 10^{-5}$	fehlt	$\sqrt{J} = 0{,}032$ bis $0{,}5$	**O2**	rel. zuv.	L21
pK_1 2,05 pK_2 4,95 (pK_1–pK_2 2,75)	25	$J = 0{,}0118$ für pK_1 $J = 0{,}108$ für pK_2	**E3b** **D3**	rel. zuv. pK_1–pK_2 wurde unabhängig bestimmt.	K13a
				Weitere Messungen: H3 (ohne exper. Angaben); B33.	

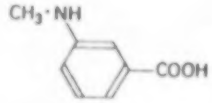
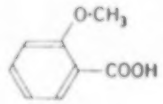
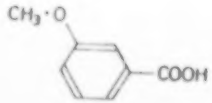
477 *m*-Amino-Benzoesäure:



pK_1 3,07 pK_2 4,73	25	$J = 0{,}012$ für pK_1 $J = 0{,}108$ für pK_2	**E3b** **D3**	rel. zuv.	K13a
K_1 $8{,}85 \cdot 10^{-4}$ K_2 $2{,}52 \cdot 10^{-5}$	25	$c = 0{,}005$	**E3a** **D1**	unsicher. Sulfat der Aminosäure wurde verwendet.	C18
				Weitere Messung: H3 (ohne exper. Angaben).	

478 *p*-Amino-Benzoesäure:

K_1 $5{,}13 \cdot 10^{-3}$ K_2 $1{,}37 \cdot 10^{-5}$	fehlt	$\sqrt{J} = 0{,}03$ bis $0{,}5$	**O2**	rel. zuv.	L21
pK_1 2,38 pK_2 4,89 (pK_1–pK_2 2,51)	25	$J = 0{,}012$ für pK_1 $J = 0{,}108$ für pK_2	**E3b** **D3**	rel. zuv. pK_1–pK_2 wurde unabhängig bestimmt.	K13a
pK_1 2,30 pK_2 4,64	fehlt	fehlt	**E3b**	unsicher. Nicht auf $J = 0$ extrapoliert, besondere Auswerteverfahren.	F1
				Weitere Messung: H3 (ohne exper. Angaben).	

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
479	*N*-Methyl-*m*-Amino-Benzoesäure: 					
	K_1 2,80·10^{-4}	25	ϵ = 0,005	**E3a** **D1**	unsicher. Sulfat der Aminosäure wurde verwendet.	C18
			216			
480	*o*-Methoxy-Benzoesäure: 					
	8,06·10^{-5}	fehlt	$\varkappa$ = 0,9 bis 1 ϵ = 0,0007 bis 0,005	**L1** **R1a** **K2e**	rel. zuv. Wie bei *o*-Tolylsäure (D14).	D14
	pK 4,08	20		**E3b** **D1**	rel. zuv.	J10
481	*m*-Methoxy-Benzoesäure: 					

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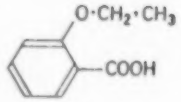
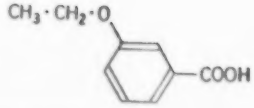
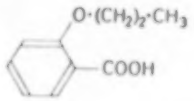
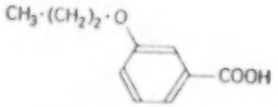
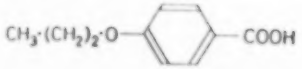
	$8{,}17 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0008$ bis $0{,}0036$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *p*-Tolylsäure (D15)	D15
	pK 4,11	20		**E3b** **D1**	rel. zuv.	J10
482	*p*-Methoxy-Benzoesäure:					
	$3{,}38 \cdot 10^{-5}$	25	$c = 0{,}0003$ bis $0{,}0007$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Benzoesäure (D18).	D18
	pK 4,52	20		**E3b** **D1**	rel. zuv.	J10
483	*o*-Äthoxy-Benzoesäure: 					
	pK 4,21	20		**E3b** **D1**	rel. zuv.	J10
484	*m*-Äthoxy-Benzoesäure: 					
	pK 4,17	20		**E3b** **D1**	rel. zuv.	J10

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
485	*p*-Äthoxy-Benzoesäure:					
	pK 4,480	20		**E3b** **D1**	rel. zuv.	J10
486	*o*-n-Propyl-oxy-Benzoesäure: 					
	pK 4,24	20		**E3b** **D1**	rel. zuv.	J10
487	*m*-n-Propyl-oxy-Benzoesäure: 					
	pK 4,20	20		**E3b** **D1**	rel. zuv.	J10
488	*p*-n-Propyl-oxy-Benzoesäure: 					

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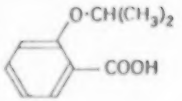
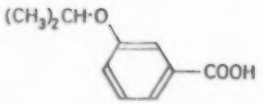
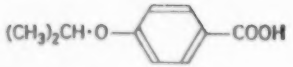
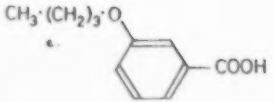
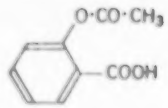
	pK' 4,78	20	**E3b** **D1**	rel. zuv.	J10
489	*o*-iso-Propyl-oxy-Benzoesäure: 				
	pK' 4,24	20	**E3b** **D1**	rel. zuv.	J10
490	*m*-iso-Propyl-oxy-Benzoesäure: 				
	pK' 4,15	20	**E3b** **D1**	rel. zuv.	J10
491	*p*-iso-Propyl-oxy-Benzoesäure: 				
	pK' 4,68	20	**E3b** **D1**	rel. zuv.	J10
492	*m*-n-Butyl-oxy-Benzoesäure: 				
	pK' 4,25	20	**E3b** **D1**	rel. zuv.	J10

Bezeichnung 216–217

No. 493–499

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
493	*o*-Phenoxy-Benzoesäure:					
	$2{,}97 \cdot 10^{-3}$	fehlt	$\varkappa = 0{,}9$ bis 1 $\varepsilon = 0{,}00008$ bis $0{,}0005$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *o*-Tolylsäure (D14).	D14
494	*m*-Phenoxy-Benzoesäure:					
	$1{,}12 \cdot 10^{-4}$	fehlt	$\varkappa = 0{,}9$ bis 1 $\varepsilon = 0{,}0001$ bis $0{,}0002$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *o*-Tolylsäure (D14).	D14
495	*p*-Phenoxy-Benzoesäure:					
	$3{,}00 \cdot 10^{-5}$	fehlt	$\varkappa = 0{,}9$ bis 1 $\varepsilon = 0{,}00007$ bis $0{,}00015$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *o*-Tolylsäure (D14).	D14

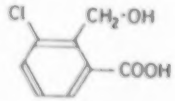
496 Acetyl-Salizylsäure (Aspirin):



$2{,}72 \cdot 10^{-3}$	17	$\mathcal{J} = 0{,}0007$ bis $0{,}1$	**O5**	rel. zuv.	E2

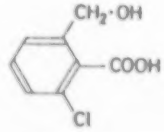
217

497 3-Chlor-2-Methylol-Benzoesäure:



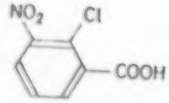
pK 3,27	20	**E3b**	unsicher. Ohne exper. Angaben.	T5

498 6-Chlor-2-Methylol-Benzoesäure:

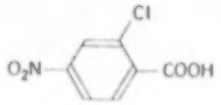
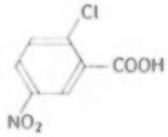
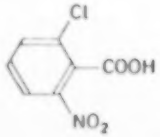


pK 2,26	20	**E3b**	unsicher. Ohne exper. Angaben.	T5

499 2-Chlor-3-Nitro-Benzoesäure:

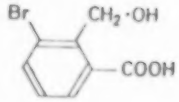


$9{,}51 \cdot 10^{-3}$	25	$c = 0{,}00005$ bis $0{,}0008$	**L1** **R1a**	rel. zuv. Parkereffekt, Wasserthermostat.	D10

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
500	2-Chlor-4-Nitro-Benzoesäure: 					
	$10{,}9 \cdot 10^{-3}$	25	$c = 0{,}00005$ bis $0{,}0008$	**L1** **R1a**	rel. zuv. Parkereffekt, Wasserthermostat.	D10
501	2-Chlor-5-Nitro-Benzoesäure: 					
	$6{,}80 \cdot 10^{-3}$	25	$c = 0{,}00005$ bis $0{,}0008$	**L1** **R1a**	rel. zuv. Parkereffekt, Wasserthermostat.	D10
502	2-Chlor-6-Nitro-Benzoesäure: 					

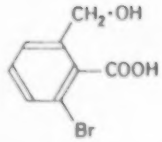
	$4{,}55 \cdot 10^{-2}$	25	$c = 0{,}00005$ bis $0{,}0008$	**L1** **R1a**	rel. zuv. Parkereffekt, Wasserthermostat.	D10

503 3-Brom-2-Methylol-Benzoesäure:



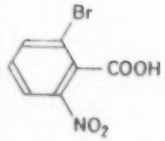
	pK 3,28	20		**E3b**	unsicher. Ohne exper. Angaben.	T5

504 6-Brom-2-Methylol-Benzoesäure:

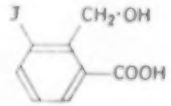
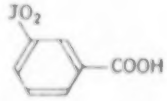


	pK 2,25	20		**E3b**	unsicher. Ohne exper. Angaben.	T5

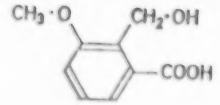
505 2-Brom-6-Nitro-Benzoesäure:



	$4{,}24 \cdot 10^{-2}$	25	$c = 0{,}00005$ bis $0{,}001$	**L1** **R1a**	rel. zuv. Parkereffekt, Wasserthermostat.	D10

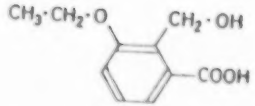
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
506	3-Jod-2-Methylol-Benzoesäure: 					
	pK 3,18	20		**E3b**	unsicher. Ohne exper. Angaben.	T5
507	*m*-Jodoxy-Benzoesäure: 					
	$2{,}52 \cdot 10^{-4}$	50	$c = 0{,}0007$ bis $0{,}0017$	**E3b**	unsicher. Wenig exper. Angaben.	B44
508	*p*-Jodoxy-Benzoesäure:					
	$2{,}88 \cdot 10^{-4}$	50	$c = 0{,}0007$ bis $0{,}0017$	**E3b**	unsicher. Unvollkommene Berücksichtigung der Aktivitätskoeffizienten.	B44

509 3-Methoxy-2-Methylol-Benzoesäure:



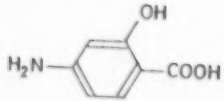
pK 3,58	20	**E3b**	unsicher. ohne exper. Angaben.	T5

510 3-Äthoxy-2-Methylol-Benzoesäure:

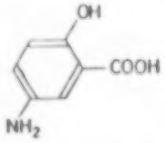
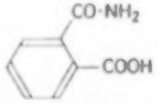
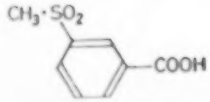


pK 3,62	20	**E3b**	unsicher. Ohne exper. Angaben.	T5

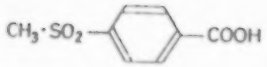
511 4-Amino-Salizylsäure:



K_1 $1{,}02 \cdot 10^{-2}$ K_2 $1{,}21 \cdot 10^{-4}$	fehlt $\mathcal{J} = 0{,}0009$ bis $0{,}25$	**O5**	rel. zuv.	L21
pK_1 1,7 pK_2 3,9	fehlt	**E3b**	unsicher. Nicht auf $\mathcal{J} = 0$ extrapoliert.	F1
			Weitere Messungen: Z1.	

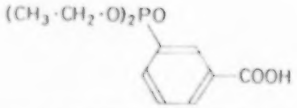
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
512	5-Amino-Salizylsaure: 					
	pK_1 2,74 pK_2 5,84	fehlt		**E3b**	unsicher. Nicht auf $J = 0$ extrapoliert.	F1
513	Phthalsaure-Monoamid: 					
	$1{,}76 \cdot 10^{-4}$	25		**L2**	unsicher. Hydrolisiert sehr leicht.	W8
514	3-Methylsulfonyl-Benzoesaure: 					
	pK 3,52	fehlt	$c = 0{,}0002$ bis $0{,}0005$	**E3a** **D1**	unsicher.	K26

515 4-Methylsulfonyl-Benzoesäure:



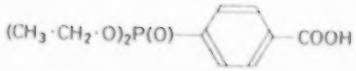
pK 3,64	fehlt	c = 0,0002 bis 0,0005	**E3a** **D1**	unsicher.	K26

516 *m*-Diäthoxyphosphinyl-Benzoesäure:



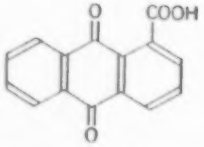
pK 3,65	23	$\mathcal{J}$ = 0,04	**E3b**	unsicher.	F5a

517 *p*-Diäthoxyphosphinyl-Benzoesäure:

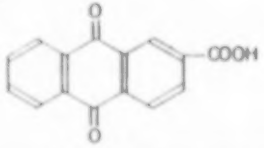
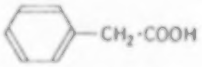


pK 3,60	23	$\mathcal{J}$ = 0,04	**E3b**	unsicher.	F5a

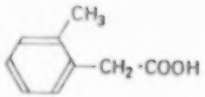
518 Anthrachinon-carbonsäure-1:



$4{,}27 \cdot 10^{-4}$	20	x = 1 c = 0,001	**E3b**	unsicher. Keine exper. Angaben.	L14

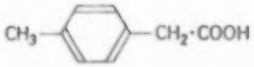
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
519	Anthrachinon-carbonsaure-2: 					
	$3{,}82 \cdot 10^{-4}$	20	$\varkappa = 1$ $c = 0{,}001$	**E3b**	unsicher. Keine exper. Angaben.	L14
			221			
520	Phenyl-Essigsäure: 					
	$4{,}86 \cdot 10^{-5}$	18	$\mathcal{J} = 0{,}008$ bis 3	**E2b**	zuv.	L11
	$4{,}88 \cdot 10^{-5}$	25	$\varkappa = 1{,}2$ $c = 0{,}0006$ bis $0{,}03$	**L1** **R1a** **K2a**	rel. zuv. Solvenskorr. unsicher; Hydrolyseneinfluß nicht diskutiert; Glaszellen; Wasserthermostat.	D17
	(c) $4{,}884 \cdot 10^{-5}$	25	$\varkappa = 0{,}7$ $\mathcal{J} = 0{,}0002$ bis $0{,}07$	**L1** **R1b** **K2d**	zuv. Parkereffekt möglich.	J4
	$4{,}88 \cdot 10^{-5}$	25	$\varkappa = 1$	**E3a** **D1**	rel. zuv. bis unsicher.	G10
	pK 4,32	25	(a) $\mathcal{J} = 0{,}01$ (b) $\mathcal{J} = 0{,}005$ bis $0{,}02$	(a) **E2c** **D1** (b) **O3**	rel. zuv. Chinhydronelektrode.	K9

521 α-Methylphenyl-Essigsäure (*o*-Tolyl-Essigsäure):



$4{,}5 \cdot 10^{-5}$	18	$\gamma = 0{,}01$ bis $0{,}03$	**E2b**	rel. zuv.	L10

522 *p*-Tolyl-Essigsäure:



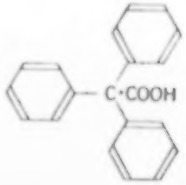
$4{,}27 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0004$ bis $0{,}002$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Acrylsäure (D13).	D13

523 *p*-Äthylphenyl-Essigsäure:

$4{,}24 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0002$ bis $0{,}0006$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *p*-tert.-Butyl-Benzoesäure (B6).	B6

524 *p*-iso-Propylphenyl-Essigsäure:

$4{,}06 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0001$ bis $0{,}0008$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *p*-tert.-Butyl-Benzoesäure (B6).	B6

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
525	*p*-tert.-Butylphenyl-Essigsäure:					
	$3{,}825 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0004$ bis $0{,}0012$	**L1** **R1a** **K2c**	rel. zuv. Wie bei *p*-tert.-Butyl-Benzoesäure (B6).	B6
526	Diphenyl-Essigsäure:					
	$1{,}15 \cdot 10^{-4}$	25	$\varkappa = 1{,}2$ $c = 0{,}00008$ bis $0{,}0003$	**L1** **R1a** **K2a**	rel. zuv. Wie bei Phenyl-Essigsäure (D17).	D17
527	Triphenyl-Essigsäure: 					

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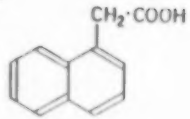
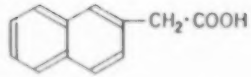
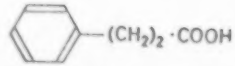
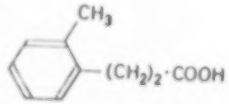
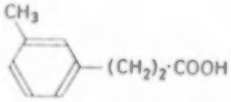
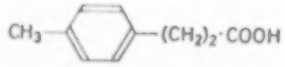
	pK 3,96	25		Losl. mssgn.	unsicher.	K9
528	α-Naphthyl-Essigsäure: 					
	$5{,}805 \cdot 10^{-5}$	25	$\varkappa = 0{,}6$ $c = 0{,}0002$ bis $0{,}002$	**L1** **R1a** **K2e**	rel. zuv. Glaszellen; Wasserthermostat; Solvenskorr. unsicher; Salzlösungen enthielten Säureüberschuß.	D11
529	β-Naphthyl-Essigsäure: 					
	$5{,}55 \cdot 10^{-5}$	25	$\varkappa = 0{,}6$ $c = 0{,}00025$ bis $0{,}0012$	**L1** **R1a** **K2e**	rel. zuv. Wie bei α-Naphthyl-Essigsäure (D11).	D11
530	β-Phenyl-Propionsäure: 					
	$2{,}19 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0008$ bis $0{,}004$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Acrylsäure (D13).	D13
	$2{,}16 \cdot 10^{-5}$	18	$\mathcal{J} = 0{,}005$ bis 3	**E2b**	rel. zuv. Reinheit der Säure ungewiß.	L11

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
531	β-(*o*-Tolyl)-Propionsäure: 					
	$2{,}17 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0003$ bis $0{,}001$	**L1** **R1a** **K2e**	rel. zuv. Glaszellen; Wasserthermostat; Parkereffekt; unsichere Solvenskorr.; über Hydrolysekorr. keine Angaben.	D16
532	β-(*m*-Tolyl)-Propionsäure: 					
	$2{,}105 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0001$ bis $0{,}0005$	**L1** **R1a** **K2e**	rel. zuv. Wie β-(*o*-Tolyl)-Propionsäure (D16).	D16
533	β-(*p*-Tolyl)-Propionsäure: 					
	$2{,}07 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0002$ bis $0{,}0008$	**L1** **R1a** **K2e**	rel. zuv. Wie β-(*o*-Tolyl)-Propionsäure (D16).	D16

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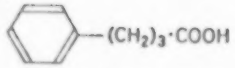
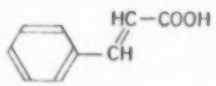
534 γ-Phenyl-n-Buttersäure:



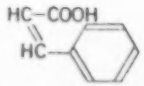
$1{,}75 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0008$ bis $0{,}004$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Acrylsäure (D13).	D13

535 *trans*-Zimtsäure:



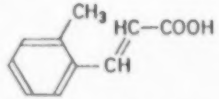
$3{,}65 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0008$ bis $0{,}003$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Acrylsäure (D13).	D13
				Weitere Messungen: H38; L3.	

536 *cis*-Zimtsäure:

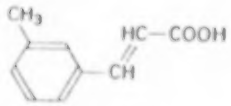
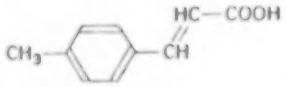
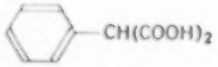


$1{,}32 \cdot 10^{-4}$	25	$\varkappa = 1$ $c = 0{,}0005$ bis $0{,}003$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Acrylsäure (D13).	D13

537 *o*-Methyl-*trans*-Zimtsäure:



$3{,}165 \cdot 10^{-5}$		$\varkappa = 0{,}9$ bis 1 $c = 0{,}00005$ bis $0{,}0001$	**L1** **R1a** **K2e**	rel. zuv. Wie bei β-(*o*-Tolyl)-Propionsäure (D16).	D16

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
538	*m*-Methyl-*trans*-Zimtsäure: 					
	$3{,}615 \cdot 10^{-5}$		$\varkappa = 0{,}9$ bis 1 $c = 0{,}0001$ bis $0{,}0006$	**L1** **R1a** **K2e**	rel. zuv. Wie bei β-(o-Tolyl)-Propionsäure (D16).	D16
539	*p*-Methyl-*trans*-Zimtsäure: 					
	$2{,}73 \cdot 10^{-5}$		$\varkappa = 0{,}9$ bis 1 $c = 0{,}00007$ bis $0{,}0001$	**L1** **R1a** **K2e**	rel. zuv. Wie bei β-(o-Tolyl)-Propionsäure (D16).	D16
540	Phenyl-Malonsäure: 					
	K_1 $2{,}65 \cdot 10^{-3}$ K_2 $9{,}4 \cdot 10^{-6}$		25	**E3b**	unsicher. Nähere Angaben fehlen.	G6

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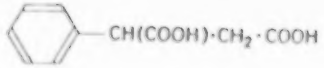
	K_1 2,77·10^{-3}	25		**L1**	unsicher. Ostwald. Verdünnungsgesetz; nähere Angaben fehlen.	B11

541 Phenyl-Bernsteinsäure:

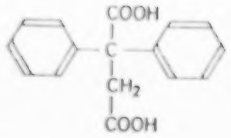


K_1 1,65·10^{-3} K_2 2,8 ·10^{-6} pK_1 3,78 pK_2 5,55	20	$\mathcal{J} \simeq 0{,}001$	**E3b** **D1** **R3d**	rel. zuv.	M23
K_1 1,65·10^{-3}	25	c = 0,0005 bis 0,02	**L**	unsicher. Nähere Angaben in H25 (nicht zugänglich).	H26

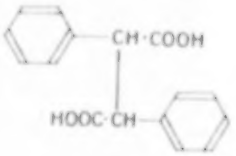
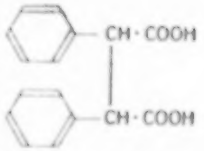
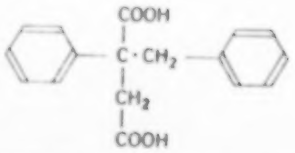
542 Benzyl-Bernsteinsäure:

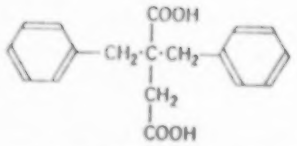
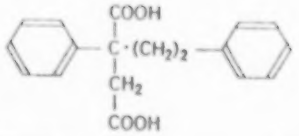
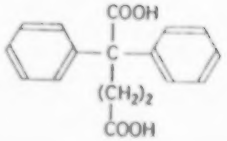
K_1 7,75·10^{-5} K_2 2,3 ·10^{-6} pK_1 4,11 pK_2 5,65	20	$\mathcal{J} \simeq 0{,}001$	**E3b** **D1** **R3d**	rel. zuv.	M23

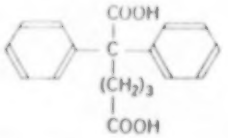
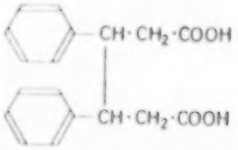
543 α,α-Diphenyl-Bernsteinsäure:



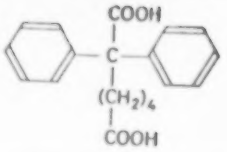
K_1 8,9·10^{-4} K_2 5·10^{-8}	20	$\mathcal{J} \simeq 0{,}001$	**E3b** **D1** **R3d**	unsicher.	M23

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
544	*rac.-α-α'*-Diphenyl-Bernsteinsäure: 					
	K_1 $2{,}65 \cdot 10^{-4}$	25	$c = 0{,}0006$ bis $0{,}01$	L.	unsicher. Nähere Angaben in H25 (unzugänglich).	H26
545	*meso-α,α'*-Diphenyl-Bernsteinsäure: 					
	K_1 $3{,}3 \cdot 10^{-4}$	25	$c = 0{,}0003$ bis $0{,}002$	L.	unsicher. Nähere Angaben in H25 (unzugänglich).	H26
546	α-Phenyl-α-Benzyl-Bernsteinsäure: 					

	K_1 $2{,}05\cdot10^{-4}$ K_2 $3{,}2\cdot10^{-7}$ pK_1 3,69 pK_2 6,47	20	$\mathcal{J} \simeq 0{,}001$	**E3b** **D1** **R3d**	rel. zuv.	M23
547	α,α-Dibenzyl-Bernsteinsäure: 					
	K_1 $1{,}09\cdot10^{-3}$ K_2 $2{,}2\cdot10^{-7}$ pK_1 3,96 pK_2 6,66	20	$\mathcal{J} \simeq 0{,}00025$	**E3b** **D1** **R3d**	unsicher.	M23
548	α-Phenyl-α-Phenäthyl-Bernsteinsäure: 					
	K_1 $1{,}8\cdot10^{-4}$ K_2 $3{,}0\cdot10^{-7}$ pK_1 3,74 pK_2 6,52	20	$\mathcal{J} \simeq 0{,}0009$	**E3b** **D1** **R3d**	unsicher.	M23
549	α,α-Diphenyl-Glutarsäure: 					

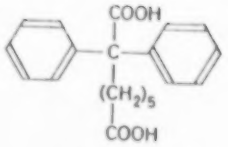
No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
	K_1 1,24·10^{-3} K_2 4,2·10^{-7} pK_1 3,91 pK_2 5,38	20	$c \simeq 0{,}001$	**E3b** **D1** **R3d**	rel. zuv.	M23
550	*α,α*-Diphenyl-Adipinsäure: 					
	K_1 6,30·10^{-5} K_2 4,0·10^{-6} pK_1 4,17 pK_2 5,40	20	$c \simeq 0{,}001$	**E3b** **D1** **R3d**	rel. zuv.	M25
551	*β,β*-Diphenyl-Adipinsäure: 					
	K_1 6,04·10^{-5} K_2 6,39·10^{-6}	25	$f \geq 0{,}001$	**E1c** **R3a**	rel. zuv.	J13
	K_1 5,31·10^{-5} K_2 4,67·10^{-6}	50				
	K_1 3,97·10^{-5} K_2 3,05·10^{-6}	74				

552 α,α-Diphenyl-Pimelinsäure:



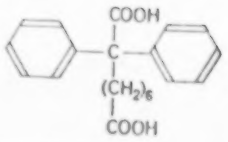
K_1 5,25·10^{-5} K_2 4,1·10^{-6} pK_1 4,28 pK_2 5,39	20	c = 0,0005	**E3b** **D1** **R3d**	rel. zuv.	M25

553 α,α-Diphenyl-Korksäure:

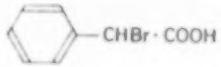
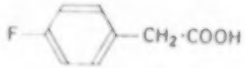
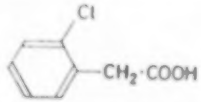
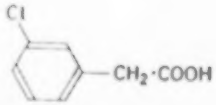


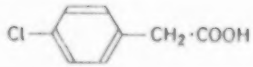
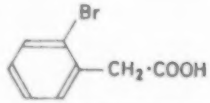
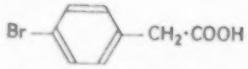
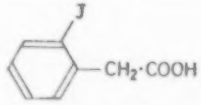
K_1 4,99·10^{-5} K_2 4,1·10^{-6} pK_1 4,31 pK_2 5,39	20	c = 0,0005	**E3b** **D1** **R3d**	rel. zuv.	M25

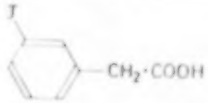
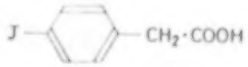
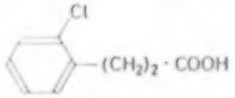
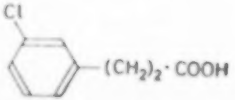
554 α,α-Diphenyl-Azelainsäure:

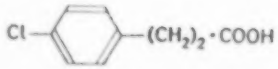
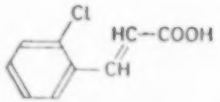
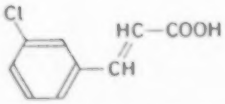


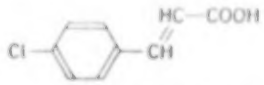
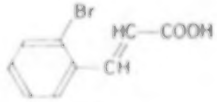
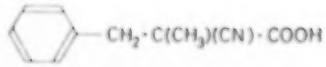
K_1 4,7·10^{-5} K_2 4,0·10^{-6} pK_1 4,33 pK_2 5,38	20	c = 0,0005	**E3b** **D1** **R3d**	unsicher.	M25

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
555	Phenyl-Brom-Essigsäure: 					
	$6{,}1 \cdot 10^{-3}$	fehlt	$f = 1$	**Kat.**	unsicher.	D8
556	*p*-Fluorphenyl-Essigsäure: 					
	$5{,}68 \cdot 10^{-5}$	25	$\varkappa = 1$ $c = 0{,}0002$ bis $0{,}003$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *o*-Chlor-Benzoesäure (D19).	D19
557	*o*-Chlorphenyl-Essigsäure: 					
	$8{,}60 \cdot 10^{-5}$	25	$\varkappa = 0{,}8$ bis $1{,}1$ $c = 0{,}003$ bis $0{,}004$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Benzoesäure (D18).	D18
					Weitere Messung: K_c-Werte. B29.	
558	*m*-Chlorphenyl-Essigsäure: 					

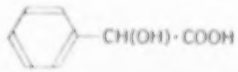
	$7{,}24 \cdot 10^{-5}$	25	$\varkappa = 0{,}8$ bis 1,1 $c = 0{,}0003$ bis 0,004	**L1** **R1a** **K2e**	rel. zuv. Wie bei Benzoesäure (D18).	D18
559	*p*-Chlorphenyl-Essigsäure: 					
	$6{,}45 \cdot 10^{-5}$	25	$\varkappa = 1{,}2$ $c = 0{,}0004$ bis 0,004	**L1** **R1a** **K2e**	rel. zuv. Wie bei Phenyl-Essigsäure (D17).	D17
560	*o*-Bromphenyl-Essigsäure: 					
	$8{,}84 \cdot 10^{-5}$	25	$\varkappa = 0{,}8$ bis 1,1 $c = 0{,}0003$ bis 0,002	**L1** **R1a** **K2e**	rel. zuv. Wie bei Benzoesäure (D18).	D18
					Weitere Messungen: K_c-Werte. B29.	
561	*p*-Bromphenyl-Essigsäure: 					
	$6{,}49 \cdot 10^{-5}$	25	$\varkappa = 1{,}2$ $c = 0{,}0002$ bis 0,003	**L1** **R1a** **K2a**	rel. zuv. Wie bei Phenyl-Essigsäure (D17).	D17
562	*o*-Jodphenyl-Essigsäure: 					
	$9{,}16 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}00025$ bis 0,0014	**L1** **R1a** **K2e**	rel. zuv. Wie bei *p*-Tolylsäure (D15).	D15

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
563	*m*-Jodphenyl-Essigsäure: 					
	$6{,}93 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0002$ bis 0,002	**L1** **R1a** **K2e**	rel. zuv. Wie bei *p*-Tolylsäure (D15).	D15
564	*p*-Jodphenyl-Essigsäure: 					
	$6{,}64 \cdot 10^{-5}$	25	$\varkappa = 1{,}2$ $c = 0{,}0002$ bis 0,0012	**L1** **R1a** **K2a**	rel. zuv. Wie bei Phenyl-Essigsäure (D17).	D17
565	*β*-(*o*-Chlorphenyl)-Propionsäure: 					
	$2{,}65 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0002$ bis 0,0007	**L1** **R1a** **K2e**	rel. zuv. Wie bei *β*-(*o*-Tolyl)-Propionsäure (D16).	D16
566	*β*-(*m*-Chlorphenyl)-Propionsäure: 					

	$2{,}60 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0002$ bis $0{,}0004$	**L1** **R1a** **K2e**	rel. zuv. Wie bei β-(*o*-Tolyl)-Propionsäure (D16).	D16
567	β-(*p*-Chlorphenyl)-Propionsäure: 					
	$2{,}47 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0001$ bis $0{,}0005$	**L1** **R1a** **K2e**	rel. zuv. Wie bei β-(*o*-Tolyl)-Propionsäure (D16).	D16
568	*o*-Chlor-*trans*-Zimtsäure: 					
	$3{,}9 \cdot 10^{-5}$	25		**E3b**	unsicher. Nähere Angaben fehlen.	B27
	$5{,}83 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}00007$ bis $0{,}0001$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *o*-Tolylsäure (D14).	D14
					Weitere Messungen: K_c-Werte. B26.	
569	*m*-Chlor-*trans*-Zimtsäure: 					
	$5{,}085 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0001$ bis $0{,}00015$	**L1** **R1a** **K2e**	rel. zuv. Wie bei β-(*o*-Tolyl)-Propionsäure (D16).	D16

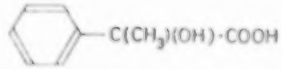
No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
570	*p*-Chlor-*trans*-Zimtsäure: 					
	$3{,}38 \cdot 10^{-5}$	25	$\alpha = 0{,}9$ bis 1 $c = 0{,}00006$ bis $0{,}00007$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *o*-Tolylsäure (D14).	D14
571	*o*-Brom-*trans*-Zimtsäure: 					
	$3{,}9 \cdot 10^{-5}$	25		**E3b**	unsicher. Nähere Angaben fehlen.	B27
572	*o*-Benzyl-*o*-Cyan-Propionsäure: 					
	$5{,}134 \cdot 10^{-3}$	25	$c = 0{,}002$ bis $0{,}003$	**L2** **R1c**	rel. zuv.	W9

223

573	Mandelsäure: 					

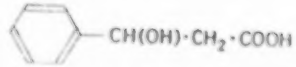
	(a) (*l*) 3,891·10⁻⁴ (b) (*dl*) 3,878·10⁻⁴	25 25	$\varkappa$ = 4,4 bis 7,9 c = 0,0001 bis 0,006	**L1** **K1f**	zuv. Säure nicht ganz rein. Mängel: Zelltyp, Solvenskorr.	B9
	4,09·10⁻⁴	18	$\mathcal{J}$ = 0,01 bis 0,03	**E2b**	zuv.	L11

574 *α*-Phenyl-*α*-Oxy-Propionsäure:



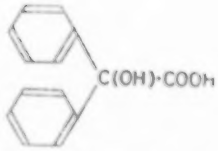
2,94·10⁻⁴	18	$\mathcal{J}$ = 0,01 bis 0,03	**E2b**	zuv.	L10

575 *β*-Phenyl-*β*-Oxy-Propionsäure:



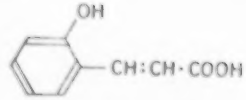
4,0·10⁻⁵	18	$\mathcal{J}$ = 0,01 bis 0,03	**E2b**	zuv.	L10

576 Benzilsäure:

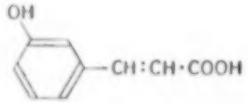
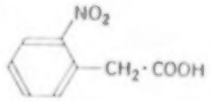
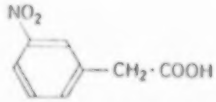


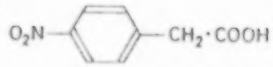
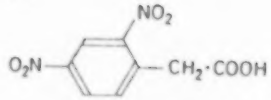
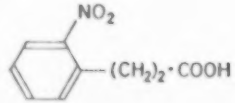
8,9·10⁻⁴	18	$\mathcal{J}$ = 0,004 bis 0,002	**E2b**	zuv.	L11

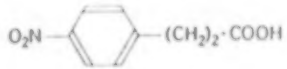
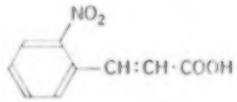
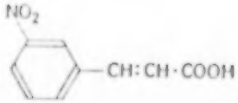
577 *o*-Oxy-Zimtsäure:



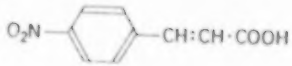
2,43·10⁻⁵	25	$\varkappa$ = 0,9 bis 1 c = 0,0002 bis 0,0006	**L1** **R1a** **K2e**	unsicher.	D16

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
578	*m*-Oxy-Zimtsäure: 					
	$4{,}02 \cdot 10^{-5}$	25	$\varkappa = 0{,}3$ bis 1 $c = 0{,}0002$ bis $0{,}0006$	**L1** **R1a** **K2c**	unsicher.	D16
			224			
579	*o*-Nitrophenyl-Essigsäure: 					
	$9{,}90 \cdot 10^{-5}$		$\varkappa = 0{,}9$ bis 1 $c = 0{,}0006$ bis $0{,}004$	**L1** **R1a** **K2c**	rel. zuv.	D14
580	*m*-Nitrophenyl-Essigsäure: 					

	$1{,}08 \cdot 10^{-4}$	25	$\varkappa = 0{,}8$ bis $1{,}1$ $c = 0{,}0005$ bis $0{,}006$	**L1** **R1a** **K2e**	rel. zuv.	D18
581	*p*-Nitrophenyl-Essigsäure: 					
	$1{,}41 \cdot 10^{-4}$	25	$\varkappa = 1{,}2$ $c = 0{,}0005$ bis $0{,}0007$	**L1** **R1a** **K2a**	rel. zuv.	D17
	$1{,}04 \cdot 10^{-4}$	25		**L1**	unsicher. Ohne nähere Angaben; nach Ostwald'schem Verdünnungsgesetz.	B11
582	2,4-Dinitrophenyl-Essigsäure: 					
	$3{,}15 \cdot 10^{-4}$	25	$\varkappa = 0{,}8$ bis $1{,}1$ $c = 0{,}0003$ bis $0{,}002$	**L1** **R1a** **K2e**	rel. zuv.	D18
583	*β*-(*o*-Nitrophenyl)-Propionsäure: 					
	$3{,}135 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0001$ bis $0{,}0004$	**L1** **R1a** **K2e**	rel. zuv.	D16

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
584	*β*-(*p*-Nitrophenyl)-Propionsäure: 					
	$3{,}365 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0001$ bis $0{,}0003$	**L1** **R1a** **K2e**	rel. zuv.	D16
585	*o*-Nitro-Zimtsäure: 					
	$7{,}07 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0008$ bis $0{,}0003$	**L1** **R1a** **K2e**	rel. zuv.	D16
586	*m*-Nitro-Zimtsäure: 					
	$7{,}58 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}00008$ bis $0{,}0001$	**L1** **R1a** **K2e**	rel. zuv.	D16

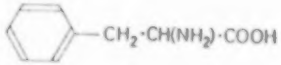
587 *p*-Nitro-Zimtsäure:



$8{,}99 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}00004$ bis $0{,}00007$	**L1** **R1a** **K2e**	rel. zuv.	D16

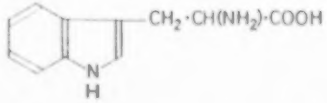
225

588 Phenyl-Alanin:

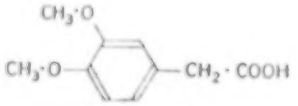
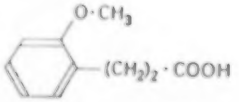


K_1 $5{,}82 \cdot 10^{-2}$ K_2 $3{,}83 \cdot 10^{-12}$	25		Angaben fehlen.	unsicher.	M22
pK_1 2,16 pK_2 9,12	24	$\mathcal{J} = 0{,}12$	**E3b**	rel. zuv.	B24
pK_1 2,16 pK_2 9,15	25	$\mathcal{J} = 0{,}05$ bis $0{,}2$	**E3b**	rel. zuv.	N3

589 Tryptophan:



K_1 $4{,}20 \cdot 10^{-3}$ K_2 $4{,}05 \cdot 10^{-10}$	25		**E3b**	unsicher. Keine näheren Angaben.	S11

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
590	*p*-Methoxyphenyl-Essigsäure:					D18
	$4{,}36 \cdot 10^{-5}$	25	$\varkappa = 0{,}8$ bis 1 $c = 0{,}0003$ bis $0{,}002$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Benzoesäure (D18).	
591	3,4-Dimethoxyphenyl-Essigsäure 					
	$4{,}64 \cdot 10^{-5}$	25	$\varkappa = 0{,}8$ bis 1 $c = 0{,}0001$ bis $0{,}004$	**L1** **R1a** **K2e**	rel. zuv. Wie bei Benzoesäure (D18).	D18
592	*β*-(*o*-Methoxyphenyl)-Propionsäure: 					
	$1{,}57 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}0002$ bis $0{,}0005$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *β*-(*o*-Tolyl)-Propionsäure (D16).	D16

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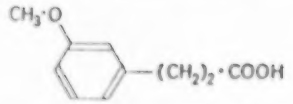
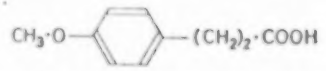
593 *β*-(*m*-Methoxyphenyl)-Propionsäure:



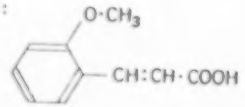
$2{,}22 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $\epsilon = 0{,}0001$ bis $0{,}0005$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *β*-(*o*-Tolyl)-Propionsäure (D16).	D16

594 *β*-(*p*-Methoxyphenyl)-Propionsäure:



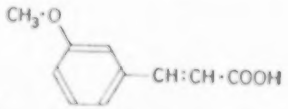
$2{,}04_5 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $\epsilon = 0{,}0002$ bis $0{,}0006$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *β*-(*o*-Tolyl)-Propionsäure (D16).	D16

595 *o*-Methoxy-Zimtsäure:

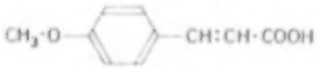
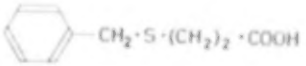
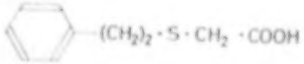
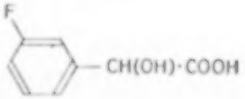


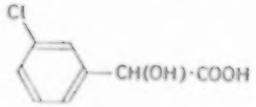
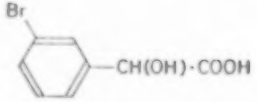
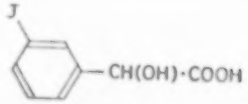
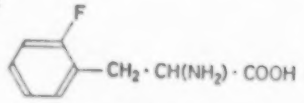
$3{,}45 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $\epsilon = 0{,}00008$ bis $0{,}00013$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *β*-(*o*-Tolyl)-Propionsäure (D16).	D16

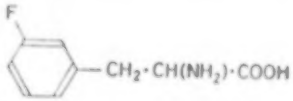
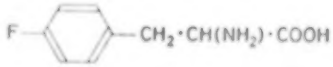
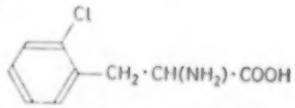
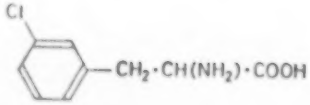
596 *m*-Methoxy-Zimtsäure:



$4{,}21 \cdot 10^{-5}$	25	$\varkappa = 0{,}9$ bis 1 $\epsilon = 0{,}0001$ bis $0{,}0004$	**L1** **R1a** **K2e**	rel. zuv. Wie bei *β*-(*o*-Tolyl)-Propionsäure (D16).	D16

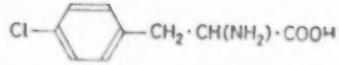
No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
597	*p*-Methoxy-Zimtsäure: 					
	$2{,}89 \cdot 10^{-4}$	25	$\varkappa = 0{,}9$ bis 1 $c = 0{,}00006$ bis $0{,}0001$	**L1** **R1a** **K2e**	rel. zuv. Wie bei β-(*o*-Tolyl)-Propionsäure (D16).	D16
			227			
598	β-(Benzyl-thio)-Propionsäure: 					
	$3{,}44 \cdot 10^{-5}$	18	$\varkappa = 0{,}7$ bis 2 $f = 0{,}004$ bis $0{,}1$	**E3b** **D1**	rel. zuv.	A7
599	Phenäthyl-thio-Essigsäure: 					
	$1{,}485 \cdot 10^{-3}$	18	$\varkappa = 0{,}7$ bis 2 $c = 0{,}004$ bis 1	**E3b** **D3**	rel. zuv.	A7
600	*m*-Fluor-Mandelsäure: 					

	$5{,}70\cdot10^{-5}$	25	$\varkappa = 1$ $\epsilon = 0{,}0007$ bis $0{,}005$	**L1** **R1a**	rel. zuv. Salze in Lösung unstabil.	G21
601	*m*-Chlor-Mandelsäure: 					
	$5{,}80\cdot10^{-4}$	25	$\varkappa = 1$ $\epsilon = 0{,}001$ bis $0{,}005$	**L1** **R1a**	rel. zuv. Salze in Lösung unstabil.	G21
602	*m*-Brom-Mandelsäure: 					
	$5{,}89\cdot10^{-4}$	25	$\varkappa = 1$ $\epsilon = 0{,}001$ bis $0{,}005$	**L1** **R1a**	rel. zuv. Salze in Lösung unstabil.	G21
603	*m*-Jod-Mandelsäure: 					
	$5{,}15\cdot10^{-4}$	25	$\varkappa = 1$ $\epsilon = 0{,}001$ bis $0{,}005$	**L1** **R1a**	rel. zuv. Salze in Lösung unstabil.	G21
604	*o*-Fluorphenyl-Alanin: 					
	pK_1 2,12 pK_2 9,01	24	$\mathcal{J} = 0{,}05$ bis $0{,}2$	**E3b** **D1**	rel. zuv.	B24

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
605	*m*-Fluorphenyl-Alanin: 					
	pK_1 2,10 pK_2 8,98	24	I = 0,05 bis 0,2	**E3b** **D1**	rel. zuv.	B24
606	*p*-Fluorphenyl-Alanin: 					
	pK_1 2,13 pK_2 9,05	24	I = 0,05 bis 0,2	**E3b** **D1**	rel. zuv.	B24
607	*o*-Chlorphenyl-Alanin: 					
	pK_1 2,23 pK_2 8,94	25	I = 0,07 bis 0,2	**E3b** **D1**	rel. zuv.	N3
608	*m*-Chlorphenyl-Alanin: 					

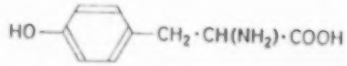
	pK_1 2,17 pK_2 8,91	25	$\mathcal{J} = 0{,}07$ bis 0,2	**E3b** **D1**	rel. zuv.	N3

609 *p*-Chlorphenyl-Alanin:



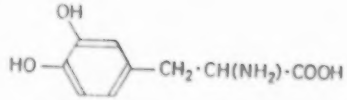
	pK_1 2,08 pK_2 8,96	25	$\mathcal{J} = 0{,}07$ bis 0,2	**E3b** **D1**	rel. zuv.	N3

610 Tyrosin:



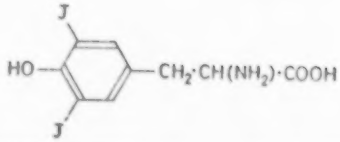
	pK_2 10,15	20	$\mathcal{J} = 0{,}04$	**O5**	rel. zuv.	C26
	pK_2 10,1		$\mathcal{J} = 0{,}01$	**O5**	unsicher.	F6

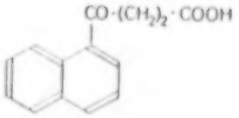
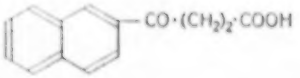
611 3,4-Dioxyphenyl-Alanin:



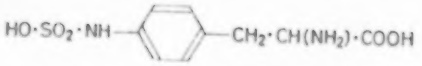
	K_1 $4{,}80 \cdot 10^{-3}$ K_2 $2{,}11 \cdot 10^{-9}$ K_3 $1{,}33 \cdot 10^{-10}$	25		**E3b** **D1**	unsicher.	M22

612 Dijod-Tyrosin:



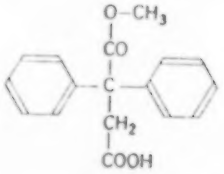
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	pK_2 6,12	20	$\mathcal{J} = 0{,}04$	**O5**	rel. zuv.	C26
	K_1 $6{,}12 \cdot 10^{-3}$ K_2 $2{,}92 \cdot 10^{-7}$ K_3 $4{,}94 \cdot 10^{-9}$	0		Lösl.- u. pH-Messgn.	rel. zuv. bis unsicher.	D20
	K_1 $7{,}63 \cdot 10^{-3}$ K_2 $3{,}32 \cdot 10^{-7}$ K_3 $1{,}51 \cdot 10^{-8}$	25				
	K_1 $7{,}85 \cdot 10^{-3}$ K_2 $3{,}51 \cdot 10^{-7}$ K_3 $3{,}56 \cdot 10^{-8}$	40				
613	*β*-(1-Naphthoyl)-Propionsäure: 					
	$3{,}3 \cdot 10^{-5}$			**E3b**	unsicher. Nähere Angaben fehlen.	N6
614	*β*-(2-Naphthoyl)-Propionsäure: 					
	$1{,}1 \cdot 10^{-5}$			**E3b**	unsicher. Nähere Angaben fehlen.	N6

615 *β*-(*p*-Sulfaminophenyl)-Alanin:



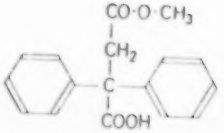
pK_1 1,99 pK_2 8,64 pK_3 10,26	25	$\mathcal{J} = 0{,}05$ bis 0,2	**E3b** **D1**	rel. zuv.	N3

616 *α*,*α*-Diphenyl-Bernsteinsäure-*α*-Methylhalbester:

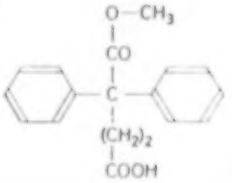
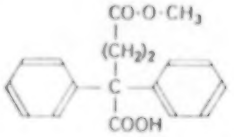
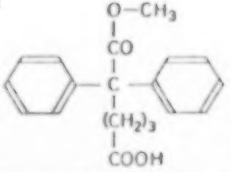


$3{,}4 \cdot 10^{-5}$	20		**E3b** **D1**	rel. zuv.	M24

617 *α*,*α*-Diphenyl-Bernsteinsäure-*β*-Methylhalbester:

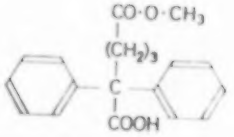


$12{,}6 \cdot 10^{-5}$	20		**E3b** **D1**	rel. zuv.	M24

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
618	α,α-Diphenyl-Glutarsäure-α-Methylhalbester: 					
	$2{,}2 \cdot 10^{-5}$	20		**E3b** **D1**	rel. zuv.	M24
619	α,α-Diphenyl-Glutarsäure-γ-Methylhalbester: 					
	$10{,}0 \cdot 10^{-5}$	20		**E3b** **D1**	rel. zuv.	M24
620	α,α-Diphenyl-Adipinsäure-α-Methylhalbester: 					

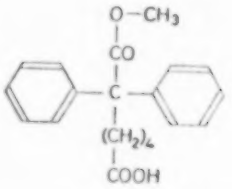
	$1{,}44 \cdot 10^{-5}$	20	**E3b** **D1**	rel. zuv.	M24

621 α,α-Diphenyl-Adipinsäure-δ-Methylhalbester:



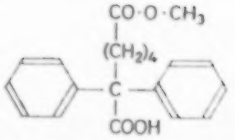
	$5{,}50 \cdot 10^{-5}$	20	**E3b** **D1**	rel. zuv.	M24

622 α,α-Diphenyl-Pimelinsäure-α-Methylhalbester:

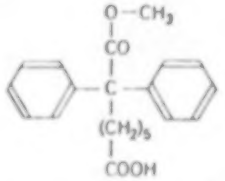
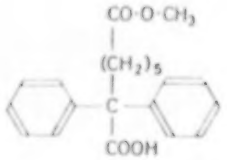
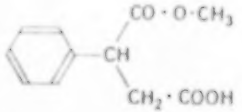


	$1{,}08 \cdot 10^{-5}$	20	**E3b** **D1**	rel. zuv.	M24

623 α,α-Diphenyl-Pimelinsäure-ε-Methylhalbester:



	$3{,}95 \cdot 10^{-5}$	20	**E3b** **D1**	rel. zuv.	M24

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
624	α,α-Diphenyl-Korksäure-α-Methylhalbester: 					
	$0{,}83 \cdot 10^{-5}$	20		**E3b** **D1**	rel. zuv.	M24
625	α,α-Diphenyl-Korksäure-ω-Methylhalbester: 					
	$3{,}15 \cdot 10^{-5}$	20		**E3b** **D1**	rel. zuv.	M24
626	α-Phenyl-Bernsteinsäure-α-Methylhalbester: 					

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$4{,}4 \cdot 10^{-5}$	20	**E3b** **D1**	rel. zuv.	M24

627 α-Phenyl-Bernsteinsäure-β-Methylhalbester:

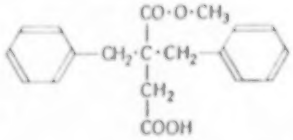
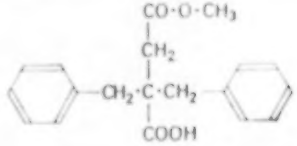
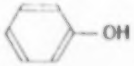
$8{,}9 \cdot 10^{-5}$	20	**E3b** **D1**	rel. zuv.	M24

628 α-Phenyl-α-Benzyl-Bernsteinsäure-α-Methylhalbester:

$3{,}5 \cdot 10^{-5}$	20	**E3b** **D1**	rel. zuv.	M24

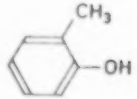
629 α-Phenyl-α-Benzyl-Bernsteinsäure-β-Methylhalbester:

$8{,}7 \cdot 10^{-5}$	20	**E3b** **D1**	rel. zuv.	M24

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
630	α,α-Dibenzyl-Bernsteinsäure-α-Methylhalbester: 					
	$2{,}2\cdot10^{-5}$	20		**E3b** **D1**	rel. zuv.	M24
631	α,α-Dibenzyl-Bernsteinsäure-β-Methylhalbester: 					
	$3{,}3\cdot10^{-5}$	20		**E3b** **D1**	rel. zuv.	M24
			31			
632	Phenol: 					
	pK 9,99	25	$\mathcal{J} = 0{,}0015$ bis 0,01	**E3a**	rel. zuv.	W1
	$pK\ 9{,}99_8$	25	$\mathcal{J} = 0{,}01$ bis 0,1	**O5**	zuv.	B36
	pK 9,98	25		**E3b**	unsicher. Nähere Angaben fehlen.	B41

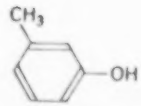
	pK' 9,88	22	c = 0,005 bis 0,01	**E3a D1**	unsicher.	K2a
	pK' 9,92	23	c = 0,00025	**O5**	unsicher.	K2a
	pK' 9,94	25	$\mathcal{J}$ = 0,02	**O5**	unsicher.	S29
	$1{,}02 \cdot 10^{-10}$	25	$\mathcal{J} \leq 0{,}01$	**E3b D1**	unsicher.	W6
	$1{,}12 \cdot 10^{-10}$	25		**O2**	rel. zuv.	J15
	$1{,}27 \cdot 10^{-10}$	25	$\mathcal{J}$ = 0,016 bis 0,05	**E1a**	rel. zuv.	A1
					Weitere Messungen: H1; H2; R9; G15. Letzteres aus Verteilungsgleichgewicht in H_2O-Cyclohexan.	

633 *o*-Kresol:



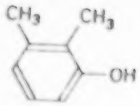
	pK' $10{,}28_7$	25	$\mathcal{J}$ = 0,01 bis 0,1	**O5**	zuv.	B36
	pK' (a) 10,15 pK' (b) 10,26 pK' (c) 10,14	25 19 23	(a) und (b): c = 0,005 bis 0,01 (c): c = 0,00025	(a) u. (b): **E3a, D1** (c): **O5**	unsicher.	(a) Glaselektrode. (b) Wasserstoffelektrode. (c) optisch. K2a
	pK' 10,28	25	$\mathcal{J}$ = 0,02	**O5**	unsicher.	S29
	pK' 10,27	17	c = 0,01	**E3b D1**	unsicher.	K2
					Weitere Messungen: G15; R9.	

634 *m*-Kresol:



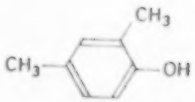
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	pK 10,091	25	$\mathcal{J} = 0{,}01$ bis 0,1	**O5**	zuv.	B36
	pK 10,08	25		**E3b**	unsicher. Nähere Angaben fehlen.	B41
	pK (a) 10,00 pK (b) 10,04 pK (c) 10,01	25 19 22	(a) u. (b): $c = 0{,}005$ bis 0,01 (c): $c = 0{,}00025$	(a) u. (b): **E3a, D1** (c): **O5**	unsicher. (a) Glaselektrode. (b) Wasserstoffelektrode. (c) optisch.	K2a
	pK 10,10	18	$c = 0{,}01$	**E3b** **D1**	unsicher.	K2
					Weitere Messungen: G15; R9.	
635	*p*-Kresol:					
	pK $10{,}26_2$	25	$\mathcal{J} = 0{,}01$ bis 0,1	**O5**	zuv.	B36
	pK 10,25	25		**E3b**	unsicher. Nähere Angaben fehlen.	B41
	pK (a) 10,22 pK (b) 10,20 pK (c) 10,14	25 19 23	(a) u. (b): $c = 0{,}005$ bis 0,01 (c): $c = 0{,}00025$	(a) u. (b): **E3a, D1** (c): **O5**	unsicher. (a) Glaselektrode. (b) Wasserstoffelektrode. (c) optisch.	K2a
	pK 10,19	25	$\mathcal{J} = 0{,}02$	**O5**	unsicher.	S29
	pK 10,35	16	$c = 0{,}01$	**E3b** **D1**	unsicher.	K2
					Weitere Messungen: G15; R9.	

636 2,3-Dimethyl-Phenol:



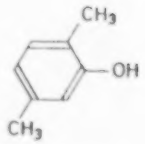
pK 10,60	18	$c = 0{,}01$	**E3b**	unsicher.		K2
pK (a) 10,50 pK (b) 10,49 pK (c) 10,42	25 16 22	(a) u. (b): $c = 0{,}005$ bis 0,01 (c): $c = 0{,}00025$	(a) u. (b): **E3a, D1** (c): **O5**	unsicher.	(a) Glaselektrode. (b) Wasserstoffelektrode. (c) optisch.	K2a

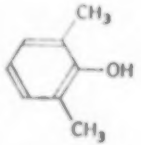
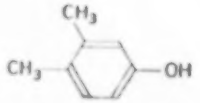
637 2,4-Dimethyl-Phenol:



pK 10,61	17,5	$c = 0{,}005$ bis 0,01	**E3a** **D1**	unsicher.		K2a
pK 10,45	25	$c = 0{,}00025$	**O5**	unsicher.		K2a
pK 10,4	28		Vertlgs.-Gleichgew. H_2O–C_6H_{12}	unsicher.		G15
pK 10,58	25	$\mathcal{J} = 0{,}02$	**O5**	unsicher.		S29

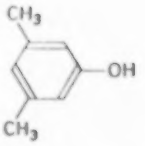
638 2,5-Dimethyl-Phenol:



No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*		*Kritik*	*Lit.*
	pK 10,21	16	$c = 0{,}005$ bis 0,01	**E3a** **D1**	unsicher.		K2a
	pK 10,22	24	$c = 0{,}00025$	**O5**	unsicher.		K2a
	pK 10,3	28		Vertlgs.-Gleichgew. H_2O–C_6H_{12}	unsicher.		G15
639	2,6-Dimethyl-Phenol: 						
	pK 10,59	25	$I = 0{,}015$ bis 0,01	**E3a**	rel. zuv.		W1
	pK 10,5	28		Vertlgs.-Gleichgew. H_2O–C_6H_{12}	unsicher.		G15
640	3,4-Dimethyl-Phenol: 						
	pK (a) 10,32 pK (b) 10,25 pK (c) 10,26	25 16 22	(a) u. (b): $c = 0{,}005$ bis 0,01 (c): $c = 0{,}00025$	(a) u. (b): **E3a, D1** (c): **O5**	unsicher.	(a) Glaselektrode. (b) Wasserstoffelektrode. (c) optisch.	K2a

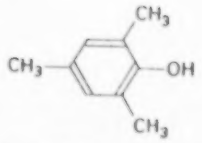
	pK 10,42	18	$c = 0{,}01$	**E3a** **D1**	unsicher.	K2

641 3,5-Dimethyl-Phenol:

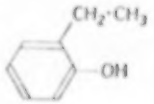
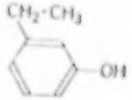
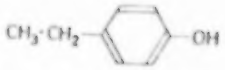


	pK 10,15	25	$\mathcal{J} = 0{,}0015$ bis $0{,}01$	**E3a** **D1**	rel. zuv.	W1
	pK (a) 10,15 pK (b) 10,13 pK (c) 10,02	25 19 24,5	(a) u. (b): $c = 0{,}005$ bis $0{,}01$ (c): $c = 0{,}00025$	(a) u. (b): **E3a, D1** (c): **O5**	unsicher.	(a) Glaselektrode. (b) Wasserstoffelektrode. (c) optisch. K2a
	pK 10,17			**E3a** **D1**	unsicher.	K26
	pK 10,0	28		Vertlgs.-Gleichgew. H_2O–C_6H_{12}	unsicher.	G15
	pK 10,25	18	$c = 0{,}01$	**E3b** **D1**	unsicher.	K2

642 2,4,6-Trimethyl-Phenol:



	pK 10,88	25	$\mathcal{J} = 0{,}02$	**O5**	unsicher.	S29

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
643	*o*-Äthyl-Phenol:  pK 10,2	28		Verthgs.-Gleichgew. H_2O-C_6H_{12} unsicher.		G15
644	*m*-Äthyl-Phenol:  pK 9,9	28		Verthgs.-Gleichgew. H_2O-C_6H_{12} unsicher.		G15
645	*p*-Äthyl-Phenol:  pK 10,0	28		Verthgs.-Gleichgew. H_2O-C_6H_{12} unsicher.		G15

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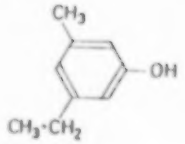
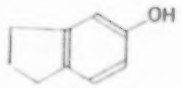
646 3-Methyl-5-Äthyl-Phenol:



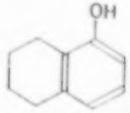
pK 10,1	28		Vertlgs.-Gleichgew. H_2O–C_6H_{12}	unsicher.	G15

647 Indanol-4:

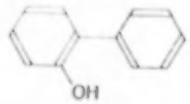
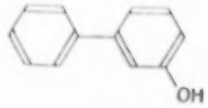


pK (a) 10,32 pK (b) 10,27 pK (c) 10,24	25 16 23	(a) u. (b): $c = 0{,}005$ bis 0,01 (c): $c = 0{,}00025$	(a) u. (b): **E3a, D1** (c): **O5**	unsicher.	(a) Glaselektrode. (b) Wasserstoffelektrode. (c) optisch.	K2a

648 Tetralol-1:



pK (a) 10,28 pK (b) 10,32 pK (c) 10,29	25 16 22	(a) u. (b): $c = 0{,}005$ bis 0,01 (c): $c = 0{,}00025$	(a) u. (b): **E3a, D1** (c): **O5**	unsicher.	(a) Glaselektrode. (b) Wasserstoffelektrode. (c) optisch.	K2a
pK 10,60	17	$c = 0{,}01$	**E3a** **D1**	unsicher.		K2

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
649	Tetrahol-2:					
	pK (a) 10,48 pK (b) 10,48 pK (c) 10,32	25 16 21,5	(a) u. (b): $\epsilon = 0{,}005$ bis 0,01 (c): $\epsilon = 0{,}00025$	(a) u. (b): **E3a, D1** (c): **O5**	unsicher.	(a) Glaselektrode. (b) Wasserstoffelektrode. (c) optisch.	K2a
	pK 10,40	17	$\epsilon = 0{,}01$	**E3a** **D1**	unsicher.		K2
650	*o*-Oxy-Biphenyl: 					
	pK (a) 10,01 pK (b) 9,97	22,5 22,5	(a) $\epsilon = 0{,}005$ bis 0,01 (b) $\epsilon = 0{,}00025$	(a): **E3a,D1,** (b): **O5**	unsicher.		K2a
651	*m*-Oxy-Biphenyl: 					
	pK (a) 9,64 pK (b) 9,63	22,5 22,5	$\epsilon = 0{,}005$ bis 0,01 $\epsilon = 0{,}00025$	(a): **E3a, D1** (b): **O5**	unsicher.		K2a

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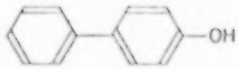
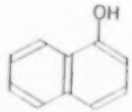
652 *p*-Oxy-Biphenyl:



pK' 9,55	22,5	c = 0,00025	**O5**	unsicher.

K2a

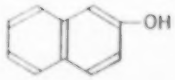
653 α-Naphthol:



pK' (a) 9,34	17,5	c = 0,005 bis 0,01	(a): **E3a, D1**	unsicher.
pK' (b) 9,30	20,5	c = 0,00025	(b): **O5**	

K2a

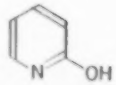
654 *β*-Naphthol:



pK' (a) 9,52	19	c = 0,005 bis 0,01	(a): **E3a, D1**	unsicher.
pK' (b) 9,57	19,5	c = 0,00025	(b): **O5**	

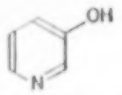
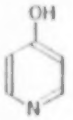
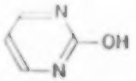
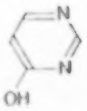
K2a

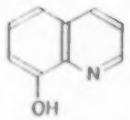
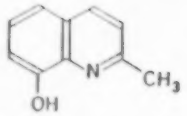
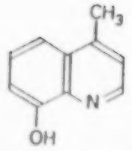
655 2-Oxy-Pyridin:

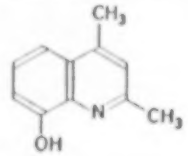
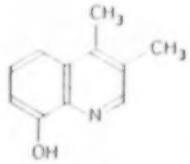
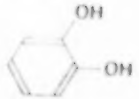


pK_2 11,62	20		**E3b**	unsicher. K_c-Werte.

A7b

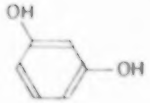
No.	Name, Formel u. Dissoziations-konstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
656	3-Oxy-Pyridin: 					
	pK_2 8,72	20		**E3b**	unsicher. K_c-Werte.	A7b
657	4-Oxy-Pyridin: 					
	pK_2 11,09	20		**E3b**	unsicher. K_c-Werte.	A7b
658	2-Oxy-Pyrimidin: 					
	pK_1 2,24 pK_2 9,17	20		**E3b**	unsicher. K_c-Werte.	A7a
659	4-Oxy-Pyrimidin: 					

	pK_1 1,85 pK_2 8,59	20		**E3b**	unsicher. K_c-Werte.	A7a
660	8-Oxy-Chinolin: 					
	pK_1 5,017 pK_2 9,813	20 25	J = 0,0036 bis 3,5	**E3b, D1** **E3c** **O5**	rel. zuv.	N1
	K_2 4,28·10^{-11} 4,20·10^{-11}	25 25		**O5** Lösl.-Messgn.	unsicher.	S33
	K_1 1,21·10^{-5} K_2 1,95·10^{-10}			**O5**	unsicher.	P6
661	8-Oxy-Chinaldin: 					
	K_1 2,84·10^{-6} K_2 4,90·10^{-11}			**O5**	unsicher.	P6
662	4-Methyl-8-Oxy-Chinolin: 					
	K_1 2,77·10^{-6} K_2 1,00·10^{-10}			**O5**	unsicher.	P6

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
663	2,4-Dimethyl-8-Oxy-Chinolin: 					
	K_1 6,34·10^{-7} K_2 2,52·10^{-11}			**O5**	unsicher.	P6
664	3,4-Dimethyl-8-Oxy-Chinolin: 					
	K_1 1,60·10^{-8} K_2 8,92·10^{-11}			**O5**	unsicher.	P26
					Weitere Messungen: (Analoge des 8-Oxy-Chinolins, Pteridine) A7a, A7b.	
665	Brenzkatechin: 					

K_1 7,50·10^{-10} K_2 8,37·10^{-13}	30	$\mathcal{I}$ = 0,001 bis 0,014	**E3b** **D1**	unsicher.	A2
K_1 1,41·10^{-10}	20	$\varkappa$ = 3 $\mathcal{I}$ = 0,03 bis 0,05	**E3a** **D1**	unsicher.	K38

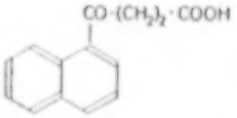
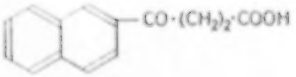
666 Resorzin:

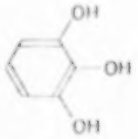
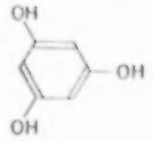
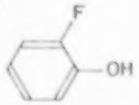


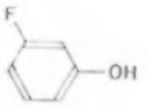
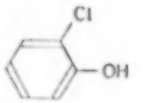
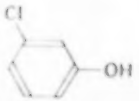
K_1 7,11·10^{-10} K_2 4,78·10^{-12}	30	$\mathcal{I}$ = 0,0005 bis 0,015	**E3b** **D1**	unsicher.	A2
K_1 1,55·10^{-10}	20	$\varkappa$ = 3 $\mathcal{I}$ = 0,03 bis 0,05	**E3a** **D1**	unsicher.	K38

667 Hydrochinon:

K_1 1,22·10^{-10} K_2 9,18·10^{-13}	30	$\mathcal{I}$ = 0,0005 bis 0,011	**E3b** **D1**	unsicher.	A2
K_1 4,47·10^{-11}	20	$\varkappa$ = 3 $\mathcal{I}$ = 0,03 bis 0,05	**E3a** **D1**	unsicher.	K38
K_1 1,06·10^{-10} 1,22·10^{-10} 1,41·10^{-11} K_2 3,20·10^{-12} 3,65·10^{-12} 4,05·10^{-12}	13,2 18,7 25 13,2 19,6 25,9	$\mathcal{I}$ = 0,65	**O5**	unsicher.	B20

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	pK_1 6,12	20	$J = 0{,}01$	**O5**	rel. zuv.	C26
	K_1 $6{,}12 \cdot 10^{-3}$ K_2 $2{,}92 \cdot 10^{-7}$ K_3 $4{,}94 \cdot 10^{-9}$	0		Leitf.- u. pH-Messgn.	rel. zuv. bis unsicher.	D20
	K_1 $7{,}65 \cdot 10^{-3}$ K_2 $3{,}32 \cdot 10^{-7}$ K_3 $1{,}51 \cdot 10^{-8}$	25				
	K_1 $7{,}85 \cdot 10^{-3}$ K_2 $3{,}51 \cdot 10^{-7}$ K_3 $3{,}56 \cdot 10^{-8}$	40				
613	*β*-(1-Naphthoyl)-Propionsäure: 					
	$3{,}3 \cdot 10^{-5}$			**E3b**	unsicher. Nähere Angaben fehlen.	N6
614	*β*-(2-Naphthoyl)-Propionsäure: 					
	$1{,}1 \cdot 10^{-5}$			**E3b**	unsicher. Nähere Angaben fehlen.	N6

	K_1 2,65·10⁻¹⁰	13,8	$\mathcal{J} = 0{,}65$	**O5**	unsicher.	B20
	3,35·10⁻¹⁰	19,9				
	4,30·10⁻¹⁰	26,4				
	K_2 7,7·10⁻¹²	13,9				
	9,6·10⁻¹²	20,1				
	11,7·10⁻¹²	26,6				
671	Pyrogallol: 					
	K_1 9,67·10⁻¹⁰		$\mathcal{J} = 0{,}0005$ bis $0{,}011$	**E3b**	unsicher.	A2
	K_2 2,30·10⁻¹²			**D1**		
672	Phloroglucin: 					
	K_1 3,56·10⁻⁹		$\mathcal{J} = 0{,}0017$ bis $0{,}0036$	**E3b**	unsicher.	A2
	K_2 1,32·10⁻⁹			**D1**		
			32			
673	*o*-Fluor-Phenol: 					
	1,55·10⁻⁹	25		**E3b**	unsicher.	B23

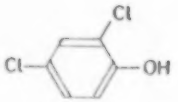
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
674	*m*-Fluor-Phenol: 					
	$5{,}25 \cdot 10^{-10}$	25		**E3b**	unsicher.	B23
675	*p*-Fluor-Phenol:					
	$1{,}12 \cdot 10^{-10}$	25		**E3b**	unsicher.	B23
	$1{,}55 \cdot 10^{-10}$	25		**O2**	rel. zuv.	J15
676	*o*-Chlor-Phenol: 					
	$7{,}73 \cdot 10^{-9}$	25	J = 0,016 bis 0,068	**E1a**	rel. zuv.	A1
	$3{,}33 \cdot 10^{-9}$	25		**O2**	rel. zuv.	J15
677	*m*-Chlor-Phenol: 					

$6{,}64 \cdot 10^{-9}$	25	$\mathcal{J} = 0{,}017$ bis $0{,}078$	**E1a**	rel. zuv.	A1
$9{,}48 \cdot 10^{-10}$	25		**O2**	rel. zuv.	J15
pK° 9,08	25		**E3b**	unsicher.	B41
				Weitere Messungen: H37.	

678 *p*-Chlor-Phenol:

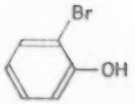
$6{,}28 \cdot 10^{-9}$	25	$\mathcal{J} = 0{,}022$ bis $0{,}09$	**E1a**	rel. zuv.	A1
$4{,}19 \cdot 10^{-10}$	25		**O2**	rel. zuv.	J15
pK° 9,42	25		**E3b**	rel. zuv.	B41

679 2,4-Dichlor-Phenol:

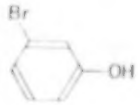
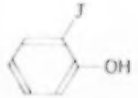


$1{,}41 \cdot 10^{-8}$	25		**O2**	rel. zuv.	J15
				Weitere Messungen über chlorierte Phenole: O3.	

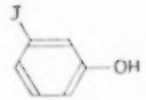
680 *o*-Brom-Phenol:



$4{,}10 \cdot 10^{-9}$	25	$\mathcal{J} = 0{,}078$ bis $0{,}085$	**E1a**	rel. zuv.	A1
$3{,}76 \cdot 10^{-9}$	25		**O2**	rel. zuv.	J15

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
681	*m*-Brom-Phenol: 					
	$1{,}36 \cdot 10^{-9}$	25	$\mathcal{I} = 0{,}022$ bis $0{,}072$	**E1a**	rel. zuv.	A1
					Weitere Messungen: H37.	
682	*p*-Brom-Phenol:					
	$5{,}65 \cdot 10^{-9}$	25	$\mathcal{I} = 0{,}019$ bis $0{,}07$	**E1a**	rel. zuv.	A1
	pK 9,34	25		**E3b**	unsicher.	B1
					Weitere Messungen über bromierte Phenole: O3.	
683	*o*-Jod-Phenol: 					
	$3{,}44 \cdot 10^{-9}$	25	$\mathcal{I} = 0{,}016$ bis $0{,}062$	**E1a**	rel. zuv.	A1

684 *m*-Jod-Phenol:



$1{,}32 \cdot 10^{-9}$	25	$\mathcal{J} = 0{,}015$ bis $0{,}065$	**E1a**	rel. zuv.	A1

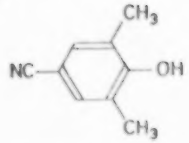
685 *p*-Jod-Phenol:

$6{,}30 \cdot 10^{-10}$	25	$\mathcal{J} = 0{,}014$ bis $0{,}068$	**E1a**	rel. zuv.	A1

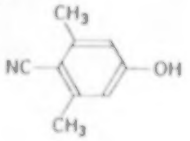
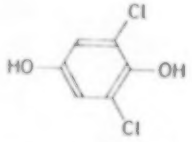
686 *p*-Cyan-Phenol:

$1{,}12 \cdot 10^{-8}$	25	$\mathcal{J} \leq 0{,}01$	**E3b** **D1**	unsicher.	W6
				Weitere Messungen: K26.	

687 2,6-Dimethyl-4-Cyan-Phenol:



$5{,}37 \cdot 10^{-9}$	25	$\mathcal{J} \leq 0{,}01$	**E3b** **D1**	unsicher.	W6

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
688	3,5-Dimethyl-4-Cyan-Phenol: 					
	$6{,}17 \cdot 10^{-9}$	25	$I \leqslant 0{,}01$	**E3b** **D1**	unsicher.	W6
					Weitere Messungen: K26.	
689	2,6-Dichlor-Hydrochinon: 					
	K_1 $4{,}20 \cdot 10^{-8}$	13,6	$I = 0{,}65$	**O5**	unsicher.	B20
	$4{,}6 \cdot 10^{-8}$	20,2				
	$5{,}0 \cdot 10^{-8}$	26,1				
	K_2 $6{,}9 \cdot 10^{-11}$	12,7				
	$8{,}7 \cdot 10^{-11}$	19,4				
	$10{,}3 \cdot 10^{-11}$	25,1				

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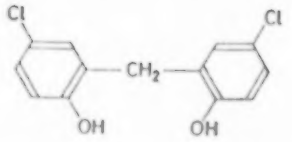
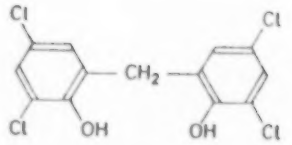
690 2,2'-Methylen-bis-(4-Chlor-Phenol):



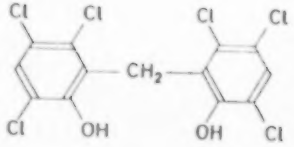
pK_1 7,6 pK_2 11,5	**O5**	unsicher.	M8

691 2,2'-Methylen-bis-(4,6-Dichlor-Phenol):

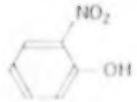
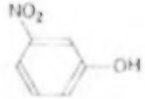


pK_1 5,6 pK_2 10,65	**O5**	unsicher.	M8

692 2,2'-Methylen-bis-(3,4,6-Trichlor-Phenol):

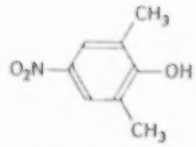


pK_2 10,1	**O5**	unsicher.	M8

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
693	*o*-Nitro-Phenol: 					
	p*K* 7,21$_6$		$\bar{J} = 0{,}01$ bis 0,1	**O5**	zuv.	B36
	5,83·10^{-8}	25		**O2**	zuv.	J15
	8,1·10^{-8}	25	$\bar{J} = 0{,}001$ bis 0,002	**E3c** **R2c**	rel. zuv.	G23
	5,9·10^{-8}	25	$c = 0{,}00003$ bis 0,001	**L1** **R1a**	rel. zuv.	D10
694	*m*-Nitro-Phenol: 					
	p*K* 8,39$_6$		$\bar{J} = 0{,}01$ bis 0,1	**O5**	zuv.	B36
	p*K* 8,38	25		**E3b**	rel. zuv.	B41
	p*K* 7,15	25		**O5**	rel. zuv.	B16
	4,51·10^{-9}	25		**O2**	zuv.	J17
695	*p*-Nitro-Phenol:					

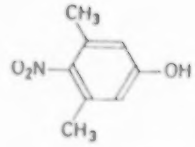
$7{,}08 \cdot 10^{-8}$	25	$\mathcal{J} = 0{,}01$ bis $0{,}09$	**O5**	rel. zuv.	B16
pK 7,149	25	$\mathcal{J} = 0{,}01$ bis $0{,}7$	**O5**	zuv.	R6
pK 6,99	25		**O5**	unsicher.	B34
pK 7,16			**E3a**	unsicher.	K26
$7{,}24 \cdot 10^{-8}$	25		**O2**	rel. zuv.	J15
$6{,}53 \cdot 10^{-8}$	25	$\mathcal{J} \leq 0{,}01$	**E3b D1**	unsicher.	W6
pK 7,16	25		**E3b D1**	unsicher.	B41

696 2,6-Dimethyl-4-Nitro-Phenol:

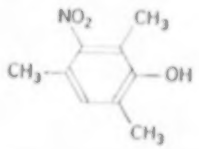
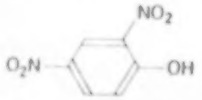
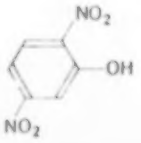


$6{,}46 \cdot 10^{-8}$	25	$\mathcal{J} \leq 0{,}01$	**E3b D1**	rel. zuv.	W1

697 3,5-Dimethyl-4-Nitro-Phenol:



$5{,}69 \cdot 10^{-9}$	25	$\mathcal{J} \leq 0{,}01$	**E3b D1**	rel. zuv.	W1
pK 8,25			**E3a**	unsicher.	K26

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
698	*m*-Nitro-Mesitol: 					
	$1{,}038 \cdot 10^{-9}$	25		**O2**	rel. zuv.	J15
699	2,4-Dinitro-Phenol: 					
	$7{,}76 \cdot 10^{-5}$	25	$\mathcal{I} = 0{,}01$ bis $0{,}09$	**O5**	rel. zuv.	B16
	$9{,}528 \cdot 10^{-5}$	25	$\mathcal{I} = 0{,}003$ bis $0{,}03$	**O2**	rel. zuv. Vergleichssäure: Glykolsäure.	M21
	pK 4,09			**O5**	unsicher.	H11
	$8{,}13 \cdot 10^{-5}$	25	$\mathcal{I} = 0{,}0001$ bis $0{,}005$	**O1**	sehr zuv.	H5
	$8{,}8 \cdot 10^{-5}$	28	$\mathcal{I} = 0{,}0025$ bis $1{,}7$	**O5**	rel. zuv. Weitere Messungen: F3.	M18
700	2,5-Dinitro-Phenol: 					

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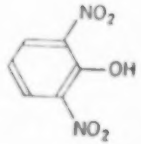
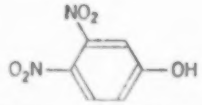
	$6{,}08 \cdot 10^{-6}$	25		**O2**	zuv. Vergleichssäure: Essigsäure.	J15
	pK 5,315	18	$\mathcal{J} = 0{,}035$ bis 3,05	**O5**	rel. zuv.	S17

701 2,6-Dinitro-Phenol:



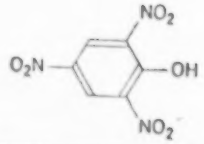
$1{,}97 \cdot 10^{-4}$	25	$c \simeq 0{,}0001$	**L1** **R1e**	rel. zuv.	D10
$1{,}940 \cdot 10^{-4}$ $1{,}938 \cdot 10^{-4}$	25 25	$\varkappa \simeq 0{,}1$ $c = 0{,}00009$ bis $0{,}00016$	**L2** **O1**	sehr zuv.	K35
$1{,}589 \cdot 10^{-4}$	25	$\mathcal{J} = 0{,}003$ bis 0,03	**O2**	rel. zuv.	M21

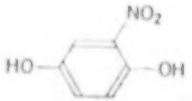
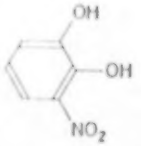
702 3,4-Dinitro-Phenol:



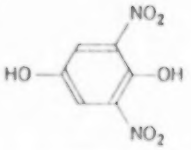
$3{,}77 \cdot 10^{-6}$	25	**O2**	zuv. Vergleichssäure: Essigsäure.	J15

703 Pikrinsäure:



No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	0,60	25	$\varkappa = 0{,}1$ $c = 0{,}00018$ bis $0{,}0043$	**L2** **R1c**	rel. zuv.	K35
	0,381	18	$c = 0{,}00198$ bis $0{,}00234$	**O1**	zuv.	H6
	0,196	25	$c \simeq 0{,}0001$	**L2** **R1c**	unsicher.	D10
	pK 0,29	25	$\mathcal{J} = 0{,}1$ bis 4	**O5**	rel. zuv. bis unsicher.	B17
704	Mononitro-Hydrochinon: 					
	pK_1 7,63 pK_2 10,06	21		**O5**	unsicher. Besondere Auswertemethode; keine Angaben über Ionenstärken.	S1
705	3-Nitro-Brenzkatechin: 					
	$2{,}1 \cdot 10^{-7}$		$\mathcal{J} = 0{,}004$	**E3b** **O5**	unsicher.	R10

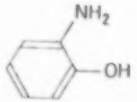
706 2,6-Dinitro-Hydrochinon:



pK_1 4,42 pK_2 9,14	21		**O5**	unsicher. Besondere Auswertemethode; keine Angaben über Ionenstärke.	S1

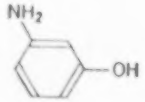
34

707 *o*-Amino-Phenol:

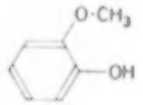
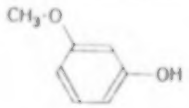


K_1 $3{,}62 \cdot 10^{-10}$ K_2 $1{,}95 \cdot 10^{-10}$	21 22	$\mathcal{I} = 0{,}37$	**E3a** **D1**	unsicher.	K38
K_1 $5{,}0 \cdot 10^{-10}$ K_2 $1{,}1 \cdot 10^{-10}$	20		**O5**	unsicher. Photographisch.	S9

708 *m*-Amino-Phenol:

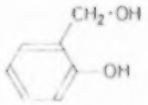


K_1 $1{,}02 \cdot 10^{-10}$ K_2 $1{,}35 \cdot 10^{-10}$	21 22	$\mathcal{I} = 0{,}37$	**E3a** **D1**	unsicher.	K38

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
709	*p*-Amino-Phenol:					
	K_1 $3{,}46 \cdot 10^{-9}$	21	$\mathcal{J} = 0{,}17$ bis $0{,}37$	**E3a**	unsicher.	K38
	K_2 $5{,}01 \cdot 10^{-11}$	22		**D1**		
			35			
710	*o*-Methoxy-Phenol: 					
	pK $9{,}98_1$		$\mathcal{J} = 0{,}01$ bis $0{,}1$	**O5**	zuv.	B36
711	*m*-Methoxy-Phenol: 					
	pK $9{,}64_9$		$\mathcal{J} = 0{,}01$ bis $0{,}1$	**O5**	zuv.	B36
	pK $9{,}65$	25		**E3b**	rel. zuv.	B41
712	*p*-Methoxy-Phenol:					

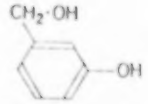
	pK 10,20$_9$		$\mathcal{J}$ = 0,01 bis 0,1	**O5**	zuv.	B36
	pK 10,20	25		**E3b**	rel. zuv.	B41

713 *o*-Methylol-Phenol:



	pK 9,92	25	$\mathcal{J}$ = 0,02	**O5**	rel. zuv.	S29

714 *m*-Methylol-Phenol:

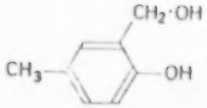


	pK 9,83	25	$\mathcal{J}$ = 0,02	**O5**	rel. zuv.	S29

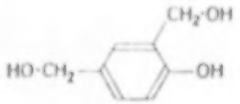
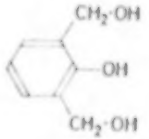
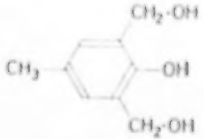
715 *p*-Methylol-Phenol:

	pK 9,82	25	$\mathcal{J}$ = 0,02	**O5**	rel. zuv.	S29

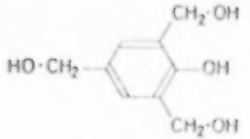
716 2-Methylol-4-Methyl-Phenol:



	pK 10,15	25	$\mathcal{J}$ = 0,02	**O5**	rel. zuv.	S29

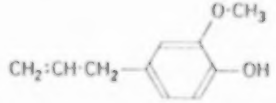
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
717	2,4-Dimethylol-Phenol: 					
	pK 9,77	25	$\mathcal{I} = 0{,}02$	**O5**	rel. zuv.	S29
718	2,6-Dimethylol-Phenol: 					
	pK 9,66	25	$\mathcal{I} = 0{,}02$	**O5**	rel. zuv.	S29
719	2,6-Dimethylol-4-Methyl-Phenol: 					
	pK 9,92	25	$\mathcal{I} = 0{,}02$	**O5**	rel. zuv.	S29

720 2,4,6-Trimethylol-Phenol:



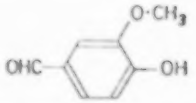
pK 9,56	25	$\gamma = 0{,}02$	**O5**	rel. zuv.	S29

721 Eugenol:



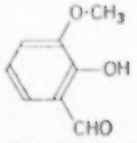
$1 \cdot 10^{-10}$	25	**L1**	unsicher.	R1

722 Vanillin:

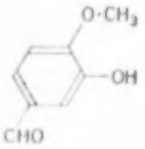
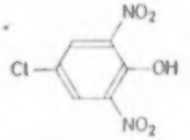
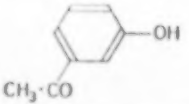


pK 7,396	25	**O5**	zuv.	R7

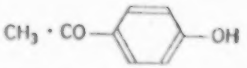
723 *o*-Vanillin:



pK 7,912	25	**O5**	zuv.	R7

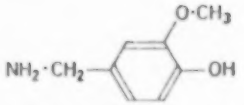
No.	*Name, Formel u. Dissoziations-Konstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
724	Isovanillin: 					
	p*K* 8,889	25		**O5**	zuv.	R7
			36			
725	4-Chlor-2,6-Dinitro-Phenol: 					
	p*K* 2,97	25		**O5**	rel. zuv.	B16
726	*m*-Oxy-Acetophenon: 					
	p*K* 9,19	25		**E3b** **D1**	rel. zuv. bis unsicher.	B41

727 *p*-Oxy-Acetophenon:



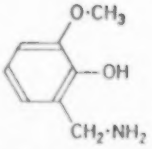
pK' 8,05	25	**E3b** **D1**	rel. zuv. bis unsicher.	B41

728 3-Oxy-2-Methoxy-Benzylamin:



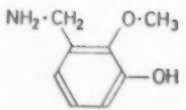
pK_1 8,94 pK_2 10,42	fehlt $J = 0{,}02$	**O5**	rel. zuv. Nähere Angaben fehlen.	R8
pK_1 8,94 pK_2 10,52		**E3b** **D1**		

729 1-Oxy-2-Methoxy-Benzylamin:

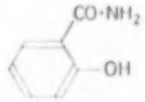
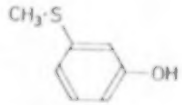
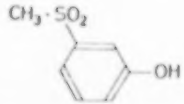


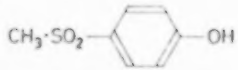
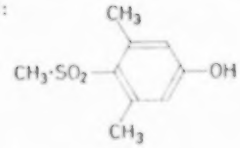
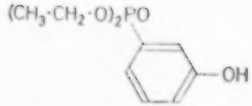
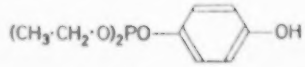
pK_1 8,70 pK_2 10,52	fehlt $J = 0{,}02$	**E3b** **D1**	rel. zuv. Nähere Angaben fehlen.	R8

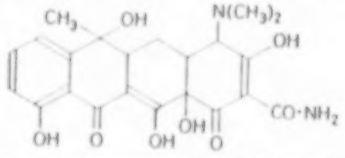
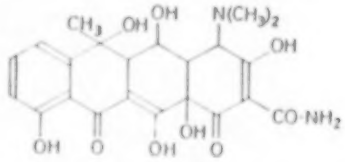
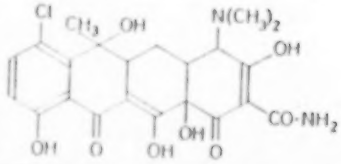
730 2-Oxy-1-Methoxy-Benzylamin:



pK_1 8,89 pK_2 10,52	fehlt $J = 0{,}02$	**E3b** **D1**	rel. zuv. Nähere Angaben fehlen.	R8

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
731	Salizylamid: 					
	$4{,}3 \cdot 10^{-9}$	20	$I = 0{,}01$ bis $0{,}2$	**O5**	unsicher.	E3
732	*m*-Methyl-thio-Phenol: 					
	pK 9,53	25		**E3b** **D1**	rel. zuv. bis unsicher.	B41
733	*p*-Methyl-thio-Phenol:					
	pK 9,53	25		**E3b** **D1**	rel. zuv. bis unsicher.	B41
734	*m*-Methylsulfonyl-Phenol: 					

	pK 9,33	25		**E3b** **D1**	rel. zuv. bis unsicher.	B41
735	*p*-Methylsulfonyl-Phenol: 					
	pK 7,83	25		**E3b** **D1**	rel. zuv. bis unsicher.	B41
	pK 7,83			**E3b** **D1**	unsicher.	K27
736	4-Methylsulfonyl-3,5-Dimethyl-Phenol: 					
	pK 8,13			**E3b** **D1**	unsicher.	K26
737	*m*-Diäthoxyphosphinyl-Phenol: 					
	pK 8,66	23	$I = 0{,}04$	**E3b**	unsicher.	F5a
738	*p*-Diäthoxyphosphinyl-Phenol: 					
	pK 8,28	23	$I = 0{,}04$	**E3b**	unsicher.	F5a

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
739	Tetracycline: 					
	pK_1 3,30 pK_2 7,68 pK_3 9,69	25	$I \simeq 0{,}1$ bis 0,01	**E3b**	rel. zuv.	S31a
740	Oxytetracycline: 					
	pK_1 3,27 pK_2 7,32 pK_3 9,11	25	$I = 0{,}1$ bis 0,01	**E3b**	rel. zuv.	S31a
741	Chlortetracycline: 					

	pK_1 3,30 pK_2 7,44 pK_3 9,27	25	$\mathcal{J}$ = 0,1 bis 0,01	**E3b**	rel. zuv.	S31a

41

742 Aminomethyl-Sulfonsäure: $NH_2{\cdot}CH_2{\cdot}SO_3H$

	pK_2 5,75			**E3**	unsicher. Ohne nähere Angaben.	R11

743 1-Aminoäthyl-Sulfonsäure: $CH_3{\cdot}CH(NH_2){\cdot}SO_3H$

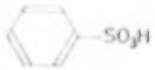
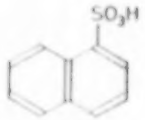
	pK_1 −0,33	25	$\mathcal{J} \leq 0{,}6$	**E1**	unsicher.	K20
	pK_2 9,4520	10	$\mathcal{J}$ = 0,02 bis 0,1	**E1a**	sehr zuv.	K20
	9,3161	15				
	9,1855	20				
	9,0614	25				
	8,9420	30				
	8,8236	35				
	8,7121	40				
	8,6042	45				
	8,4993	50				
	pK_2 9,20			**E3**	unsicher. Ohne nähere Angaben.	R11
	K_2 $1{,}8{\cdot}10^{-9}$	25	$\mathcal{J}$ = 0,1	**E3b** **D1**	unsicher.	A8

744 3-Amino-n-propyl-Sulfonsäure: $NH_2{\cdot}(CH_2)_3{\cdot}SO_3H$

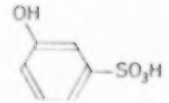
	pK_2 10,05			**E3**	unsicher. Ohne nähere Angaben.	R11

745 5-Amino-n-pentyl-Sulfonsäure: $NH_2{\cdot}(CH_2)_5{\cdot}SO_3H$

	pK_2 10,95			**E3**	unsicher. Ohne nähere Angaben	R11

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
746	10-Amino-n-decyl-Sulfonsaure: $NH_2{\cdot}(CH_2)_{10}{\cdot}SO_3H$					
	pK_2 11,35			**E3**	unsicher. Ohne nähere Angaben.	R11
747	Cysteinsaure: $COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}SO_3H$					
	K_1 $1{,}3{\cdot}10^{-2}$ K_2 $2{\cdot}10^{-9}$	25	$\varepsilon = 0{,}1$	**E3b** **D1**	unsicher.	A8
748	Phenyl-Sulfonsaure: 					
	$2{,}79_5{\cdot}10^{-3}$	25	$\bar{f} = 0{,}001$ bis $0{,}086$	**L1** **R1b**	rel. zuv.	H30
749	α-Naphthyl-Sulfonsäure: 					
	0,630	20	$\varkappa = 1$ $\varepsilon = 0{,}001$	**E3b**	unsicher. Keine experimentellen Angaben.	L14

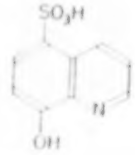
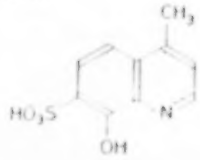
750 3-Phenol-Sulfonsäure:



pK_2 9,07	25	$\mathcal{J} = 0{,}1$	**E3b** unsicher. K_c-Werte.	Z3

751 4-Phenol-Sulfonsäure:

pK_2 8,70	25	$\mathcal{J} = 0{,}1$	**E3b** unsicher. K_c-Werte.	Z3
K_2 $4{,}45 \cdot 10^{-10}$	0	$\varkappa < 0{,}6$	**E1a** sehr zuv.	B19
5,20	5	$\mathcal{J} = 0{,}008$ bis 0,5		
6,03	10			
6,92	15			
7,85	20			
8,85	25			
9,89	30			
10,94	35			
12,00	40			
13,09	45			
14,16	50			
15,28	55			
16,33	60			
Verschiedene Naphthol-Sulfonsäuren: K_c-Werte.			Weitere Messungen: K_c-Werte.	Z3 Z2 E5a

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
752	8-Oxy-Chinolin-5-Sulfonsäure: 					
	pK_1 4,092 pK_2 8,776	25		**E3b** **D1**	rel. zuv.	N2
	K_1 $8{,}4 \cdot 10^{-5}$ K_2 $1{,}38 \cdot 10^{-9}$			**O5**	unsicher. Angaben fehlen.	P6
					Weitere Messungen: K_c-Werte. F2.	
753	4-Methyl-8-Oxy-Chinolin-7-Sulfonsäure: 					
	K_1 $1{,}67 \cdot 10^{-5}$ K_2 $0{,}976 \cdot 10^{-10}$			**O5**	unsicher. Angaben fehlen.	P6

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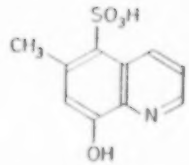
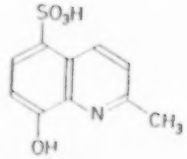
754 6-Methyl-8-Oxy-Chinolin-5-Sulfonsäure:



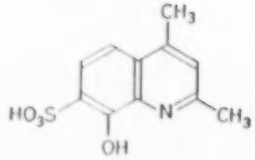
K_1 6,3·10^{-5} K_2 2·10^{-9}	**O3**	unsicher. K_c-Werte.	F2

755 8-Oxy-Chinaldin-5-Sulfonsäure:

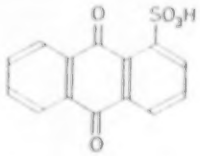
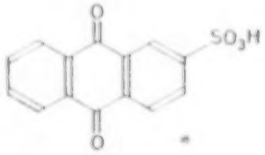
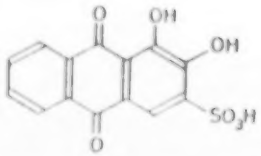


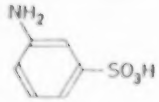
K_1 1,60·10^{-5} K_2 5,01·10^{-10}	**O5**	unsicher. Angaben fehlen.	P6

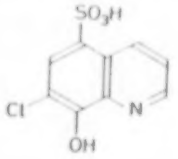
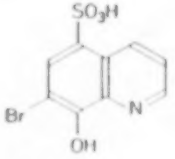
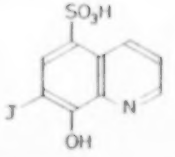
756 2,4-Dimethyl-8-Oxy-Chinolin-7-Sulfonsäure:



K_1 6,34·10^{-4} K_2 0,725·10^{-10}	**O5**	unsicher. Angaben fehlen.	P6

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
757	Anthrachinon-1-Sulfonsäure: 					
	0,540	20	$\varkappa = 1$ $\epsilon = 0{,}001$	**E3b**	unsicher. Experimentelle Angaben fehlen.	L14
758	Anthrachinon-2-Sulfonsäure: 					
	0,42	20	$\varkappa = 1$ $\epsilon = 0{,}001$	**E3b**	unsicher. Experimentelle Angaben fehlen.	L14
759	Alizarin-3-Sulfonsäure: 					

	pK_2 5,54 pK_3 11,01	19		**O5**	unsicher. Besondere indirekte Methode; wenig experimentelle Angaben.	S1
760	Metanilsäure: 					
	K_2 0,8408·10^{-4}	0	$\mathcal{I}$ = 0,01 bis 0,08	**E1a**	sehr zuv.	C24
	0,9956	5				
	1,170	10				
	1,366	15				
	1,585	20				
	1,828	25				
	2,096	30				
	2,390	35				
	2,710	40				
	3,059	45				
	3,436	50				
761	Sulfanilsäure:					
	K_2 3,016·10^{-4}	0	$\varkappa$ = 1	**E1a**	sehr zuv.	M7
	3,488	5	$\mathcal{I}$ = 0,03 bis 0,15			
	4,003	10				
	4,588	15				
	5,218	20				
	5,925	25				
	6,668	30				
	7,482	35				
	8,341	40				
	9,249	45				
	10,252	50				
	Azofarbstoffe von 1-Amino-Naphthol-6,8-Disulfonsäure.				K_c-Werte.	B38

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
762	7-Chlor-8-Oxy-Chinolin-5-Sulfonsäure: 					
	K_1 $1{,}2 \cdot 10^{-3}$ K_2 $1{,}6 \cdot 10^{-7}$			**O3**	unsicher. K_c-Werte.	F2
763	7-Brom-8-Oxy-Chinolin-5-Sulfonsäure: 					
	K_1 $3{,}1 \cdot 10^{-3}$ K_2 $2{,}0 \cdot 10^{-7}$			**O3**	unsicher. K_c-Werte.	F2
764	7-Jod-8-Oxy-Chinolin-5-Sulfonsäure: 					

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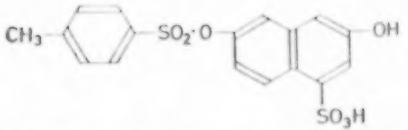
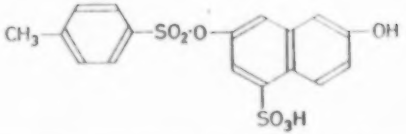
	pK_1 2,514 pK_2 7,417	25		**E3b** **D1**	rel. zuv.	N2
					Weitere Messungen: F2.	
765	2,8,6-Tolylsulfoxy-Naphthol-Sulfonsäure: 					
	pK_2 8,7	20		**E3b**	unsicher. K_c-Werte.	Z2
766	8,2,6-Tolylsulfoxy-Naphthol-Sulfonsäure: 					
	pK_2 9,6	20		**E3b**	unsicher. K_c-Werte.	Z2
			42			
	(*a*) *Phosphorsäureester*					
767	Glycerin-2-Phosphorsäureester: $CH_2(OH)\cdot CH(O\cdot PO_3H_2)\cdot CH_2\cdot OH$					
	pK_1 1,221 pK_2 6,656 pK_1 1,252 pK_2 6,650 pK_1 1,272 pK_2 6,646	5 10 15	für pK_1 $\mathcal{I} = 0{,}01$ bis 0,14 für pK_2 $\mathcal{I} = 0{,}007$ bis 0,106	**E1a**	zuv. Für die kleinen pK_1-Werte mußte Verfahren **E1a** etwas geändert werden.	A11

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
	pK_1 1,298	20				
	pK_2 6,646					
	pK_1 1,329	25				
	pK_2 6,550					
	pK_1 1,373	30				
	pK_2 6,655					
	pK_1 1,416	35				
	pK_2 6,667					
	pK_1 1,460	40				
	pK_2 6,678					
	pK_1 1,509	45				
	pK_2 6,691					
	pK_1 1,419	50				
	pK_2 6,711					
768	Glucose-1-Phosphorsäureester: $CH_2(OH)\cdot CH\cdot[CH(OH)]_2\cdot CH\cdot O\cdot PO_3H_2$ (O)					
	pK_2 6,505	5	γ = 0,01 bis 0,08	**E1a**	zuv.	A12
	6,500	10				
	6,499	15				
	6,500	20				
	6,501	25				
	6,510	30				
	6,519	35				
	6,531	40				
	6,545	45				
	6,564	50				
					Weitere Messungen: G22.	
769	Galactose-1-Phosphorsäureester: $CH_2(OH)\cdot CH\cdot[CH(OH)]_2\cdot CH\cdot O\cdot PO_3H_2$ (O)					

	pK_1 1,00 pK_2 6,17		$\mathcal{I} = 0{,}1$	**E3b**	unsicher. K_c-Werte.	K36
					Messungen an ähnlichen Stoffen: M20.	
770	2-Aminoäthanol-1-Phosphorsäureester: $NH_2{\cdot}(CH_2)_2{\cdot}O{\cdot}PO_3H_2$					
	pK_2 5,836	5	$\mathcal{I} = 0{,}003$ bis $0{,}10$	**E1a**	zuv.	G17
	5,832	10				
	5,832	15				
	5,834	20				
	5,838	25				
	5,845	30				
	5,854	35				
	5,865	40				
	5,878	45				
	5,899	50				
	(*b*) *Phosphonsäuren.*					
771	Methyl-Phosphonsäure: $CH_3{\cdot}PO_3H_2$					
	pK_1 2,38 pK_2 7,74	25	$c = 0{,}005$	**E3b** **D1**	rel. zuv.	G28
	pK_1 2,35 pK_2 7,1		$c = 0{,}1$	**E3b**	unsicher.	R12
772	Äthyl-Phosphonsäure: $CH_3{\cdot}CH_2{\cdot}PO_3H_2$					
	pK_1 2,43 pK_2 8,05	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	G28
	pK_1 2,45 pK_2 7,85		$m = 0{,}1$	**E3b**	unsicher.	R12
773	n-Propyl-Phosphonsäure: $CH_3{\cdot}(CH_2)_2{\cdot}PO_3H_2$					
	pK_1 2,49 pK_2 8,18	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	G28

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
774	iso-Propyl-Phosphonsäure: $(CH_3)_2CH{\cdot}PO_3H_2$					
	pK_1 2,66 pK_2 8,44	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	C28
775	n-Butyl-1-Phosphonsäure: $CH_3{\cdot}(CH_2)_3{\cdot}PO_3H_2$					
	pK_1 2,59 pK_2 8,19	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	C28
776	n-Butyl-2-Phosphonsäure: $CH_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}PO_3H_2$					
	pK_1 2,74 pK_2 8,48	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	C28
777	iso-Butyl-Phosphonsäure: $(CH_3)_2CH{\cdot}CH_2{\cdot}PO_3H_2$					
	pK_1 2,70 pK_2 8,43	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	C28
778	tert.-Butyl-Phosphonsäure: $(CH_3)_3C{\cdot}PO_3H_2$					
	pK_1 2,79 pK_2 8,88	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	C28
779	Neopentyl-Phosphonsäure (2,2'-Dimethyl-n-propyl-Phosphonsäure): $(CH_3)_3C{\cdot}CH_2{\cdot}PO_3H_2$					
	pK_1 2,84 pK_2 8,65	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	C28
780	tert.-Amyl-Phosphonsäure: $CH_3{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}PO_3H_2$					
	pK_1 2,88 pK_2 8,96	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	C28

781 n-Hexyl-Phosphonsäure: $CH_3 \cdot (CH_2)_5 \cdot PO_3H_2$

pK_1 2,6		$c = 0{,}1$	**E3b**	unsicher.	R12
pK_2 7,9					

782 n-Dodecyl-Phosphonsäure: $CH_3 \cdot (CH_2)_{11} \cdot PO_3H_2$

pK_2 8,25		$c = 0{,}1$	**E3b**	unsicher.	R12

783 Monochlormethyl-Phosphonsäure: $CH_2Cl \cdot PO_3H_2$

pK_1 1,40	25	$m = 0{,}005$	**E3b**	rel. zuv.	C29
pK_2 6,30			**D1**		

784 Dichlormethyl-Phosphonsäure: $CHCl_2 \cdot PO_3H_2$

pK_1 1,14	25	$m = 0{,}005$	**E3b**	rel. zuv.	C29
pK_2 5,61			**D1**		

785 Trichlormethyl-Phosphonsäure: $CCl_3 \cdot PO_3H_2$

pK_1 1,63	25	$m = 0{,}005$	**E3b**	rel. zuv.	C29
pK_2 4,81			**D1**		

786 Monobrommethyl-Phosphonsäure: $CH_2Br \cdot PO_3H_2$

pK_1 1,14	25	$m = 0{,}005$	**E3b**	rel. zuv.	C29
pK_2 6,52			**D1**		

787 Monojodmethyl-Phosphonsäure: $CH_2J \cdot PO_3H_2$

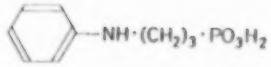
pK_1 1,30	25	$m = 0{,}005$	**E3b**	rel. zuv.	C29
pK_2 6,72			**D1**		

788 Oxymethyl-Phosphonsäure: $CH_2(OH) \cdot PO_3H_2$

pK_1 1,91	25	$m = 0{,}005$	**E3b**	rel. zuv.	C29
pK_2 7,15			**D1**		

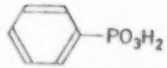
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
789	Aminomethyl-Phosphonsäure: $NH_2{\cdot}CH_2{\cdot}PO_3H_2$					
	pK_1 1,85 pK_2 5,35 pK_3 10,0			**E3b**	unsicher. K_c-Werte ohne Aktivitätskoeffizienten; nähere Angaben fehlen.	Cl4a
	pK_1 2,35 pK_2 5,9 pK_3 10,8		$\epsilon = 0{,}1$	**E3b**	unsicher.	R12
790	2-Aminoäthyl-Phosphonsäure: $NH_2{\cdot}(CH_2)_2{\cdot}PO_3H_2$					
	pK_1 2,45 pK_2 7,0 pK_3 10,8		$\epsilon = 0{,}1$	**E3b**	unsicher.	R12
791	4-Amino-n-butyl-Phosphonsäure: $NH_2{\cdot}(CH_2)_4{\cdot}PO_3H_2$					
	pK_1 2,55 pK_2 7,55 pK_3 10,9		$\epsilon = 0{,}1$	**E3b**	unsicher.	R12
792	5-Amino-n-pentyl-Phosphonsäure: $NH_2{\cdot}(CH_2)_5{\cdot}PO_3H_2$					
	pK_1 2,60 pK_2 7,6 pK_3 11,0		$\epsilon = 0{,}1$	**E3b**	unsicher.	R12
793	10-Amino-n-decyl-Phosphonsäure: $NH_2{\cdot}(CH_2)_{10}{\cdot}PO_3H_2$					
	pK_2 8,0 pK_3 11,25		$\epsilon = 0{,}02$	**E3b**	unsicher.	R12

794 3-Phenylamino-n-propyl-Phosphonsäure:



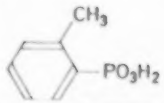
pK_2 4,25 pK_3 7,15		$c = 0,1$	**E3b**	unsicher.	R12

795 Phenyl-Phosphonsäure:



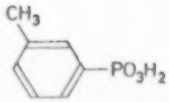
pK_1 1,83 pK_2 7,07	fehlt	$J \simeq 0,1$	**E3b** **D1**	unsicher.	J1
K_1 $1,50 \cdot 10^{-2}$ K_2 $8,51 \cdot 10^{-8}$	fehlt	$m = 0,001$	**O5**	rel. zuv. bis unsicher.	P11
pK_1 2,2 pK_2 6,85	17	$m = 0,02$	**E3b**	unsicher.	L16
				Weitere Messungen: B8.	

796 *o*-Tolyl-Phosphonsäure:

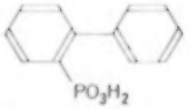
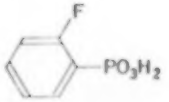


pK_1 2,10 pK_2 7,68	25	$m = 0,005$	**E3b** **D1**	rel. zuv.	C28

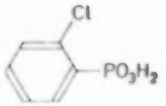
797 *m*-Tolyl-Phosphonsäure:



pK_1 1,88 pK_2 7,44	25	$m = 0,005$	**E3b** **D1**	rel. zuv.	C28

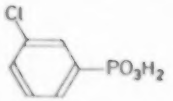
No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
798	*p*-Tolyl-Phosphonsaure:					
	pK_1 1,84 pK_2 7,33	25	$m = 0{,}005$	**E3b** **D1**	rel. zuv.	C28
	pK_1 1,78 pK_2 7,24	fehlt	$J \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
799	2-Biphenylyl-Phosphonsaure: 					
	pK_2 8,13	fehlt	$J \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
800	*o*-Fluorphenyl-Phosphonsaure: 					
	pK_1 1,64 pK_2 6,80	fehlt	$J \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

801 *o*-Chlorphenyl-Phosphonsäure:



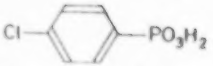
pK_1 1,63 pK_2 6,98	fehlt $\mathcal{I} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

802 *m*-Chlorphenyl-Phosphonsäure:



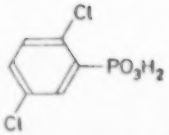
pK_1 1,55 pK_2 6,65	fehlt $\mathcal{I} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

803 *p*-Chlorphenyl-Phosphonsäure:

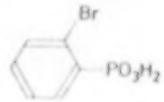
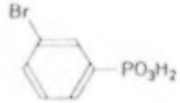


pK_1 1,66 pK_2 6,75	fehlt $\mathcal{I} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
K_1 $2{,}14 \cdot 10^{-2}$ K_2 $1{,}45 \cdot 10^{-7}$	fehlt $c = 0{,}001$	**O5**	unsicher.	P11

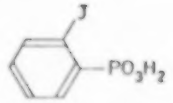
804 2,5-Dichlorphenyl-Phosphonsäure:



pK_2 6,63	fehlt $\mathcal{I} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

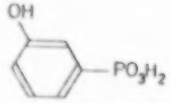
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
805	*o*-Bromphenyl-Phosphonsäure: 					
	pK_1 1,64 pK_2 7,00	fehlt	$I \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
806	*m*-Bromphenyl-Phosphonsäure: 					
	pK_1 1,45 pK_2 6,89	fehlt	$I \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
807	*p*-Bromphenyl-Phosphonsäure:					
	pK_1 2,15 pK_2 6,6	17	$I = 0{,}02$	**E3b**	unsicher.	L16
	pK_2 6,83	fehlt	$I \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
	K_1 2,51·10^{-2} K_2 2,04·10^{-7}	fehlt	$c = 0{,}001$	**O5**	unsicher.	P11

808 *o*-Jodphenyl-Phosphonsäure:



pK_1 1,74 pK_2 7,06	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

809 Phenol-3-Phosphonsäure:

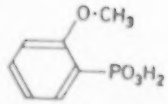


pK_1 1,78 pK_2 7,03 pK_3 10,2	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

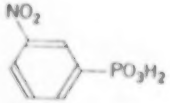
810 Phenol-4-Phosphonsäure:

pK_1 1,99 pK_2 7,25 pK_3 9,9	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

811 *o*-Methoxyphenyl-Phosphonsäure:

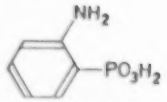


pK_1 2,16 pK_2 7,77	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
812	*p*-Methoxyphenyl-Phosphonsäure:					
	pK_1 2,4 pK_2 7,15	17	$J = 0{,}02$	**E3b**	unsicher.	L16
	K_1 $8{,}32 \cdot 10^{-3}$ K_2 $9{,}55 \cdot 10^{-8}$	fehlt	$m = 0{,}001$	**O5**	unsicher.	P11
813	*p*-Äthoxyphenyl-Phosphonsäure:					
	pK_1 2,08 pK_2 7,28	fehlt	$J \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
814	*m*-Nitrophenyl-Phosphonsäure: 					
	pK_1 1,30 pK_2 6,27	fehlt	$J \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
815	*p*-Nitrophenyl-Phosphonsäure:					

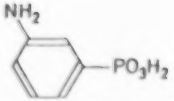
	pK_1 1,24 pK_2 6,23	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

816 *o*-Aminophenyl-Phosphonsäure:



	pK_2 4,10 pK_3 7,29	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

817 *m*-Aminophenyl-Phosphonsäure:

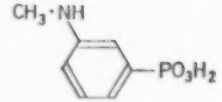


	pK_3 7,16	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

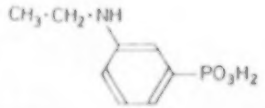
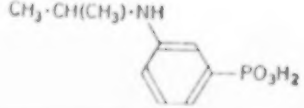
818 *p*-Aminophenyl-Phosphonsäure:

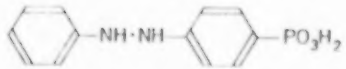
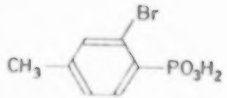
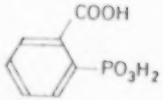
	pK_3 7,53	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

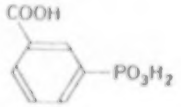
819 *m*-Methylaminophenyl-Phosphonsäure:



	pK_1 1,1 pK_2 4,72 pK_3 7,30	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
820	*p*-Methylaminophenyl-Phosphonsäure:					
	pK_3 7,85	fehlt	$I \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
821	*p*-Dimethylaminophenyl-Phosphonsäure:					
	pK_1 2,0 pK_2 4,2 pK_3 7,35	17	$I = 0{,}02$	**E3b**	unsicher.	L16
822	*m*-Äthylaminophenyl-Phosphonsäure: 					
	pK_1 1,1 pK_2 4,90 pK_3 7,24	fehlt	$I \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
823	*m*-iso-Propylaminophenyl-Phosphonsäure: 					

	pK_3 7,33	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
824	Hydrazobenzol-4-Phosphonsäure: 				
	pK_3 7,54	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
825	*p*-Acetylaminophenyl-Phosphonsäure:				
	pK_3 7,10	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
826	2-Brom-*p*-tolyl-Phosphonsäure: 				
	pK_1 1,81 pK_2 7,15	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
827	Benzoesäure-2-Phosphonsäure: 				
	pK_1 1,71 pK_2 3,78 pK_3 9,17	fehlt $\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
828	Benzoesäure-3-Phosphonsäure: 					
	pK_1 1,55 pK_2 4,03 pK_3 7,03	fehlt	$J \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
829	Benzoesäure-4-Phosphonsäure:					
	pK_1 1,50 pK_2 3,95 pK_3 6,89	fehlt	$J \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
830	*p*-Sulfamoylphenyl-Phosphonsäure:					
	pK_1 1,42 pK_2 6,38 pK_3 10,0	fehlt	$J \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

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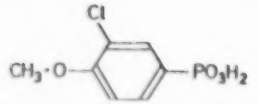
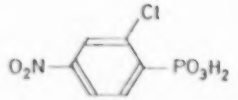
831 3-Chlor-4-Methoxyphenyl-Phosphonsäure:



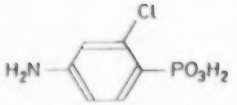
pK_1 2,25 pK_2 6,7	17	$m = 0{,}02$	**E3b**	unsicher.	L16

832 2-Chlor-4-Nitrophenyl-Phosphonsäure:



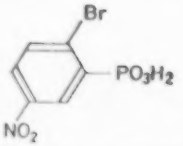
pK_1 1,12 pK_2 6,14	fehlt	$\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

833 2-Chlor-4-Aminophenyl-Phosphonsäure:

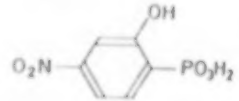
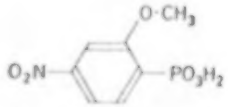
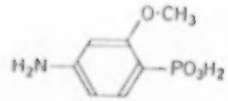


pK_2 7,33	fehlt	$\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

834 2-Brom-5-Nitrophenyl-Phosphonsäure:



pK_2 6,14	fehlt	$\mathcal{J} \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

No.	*Name, Formel u. Dissoziations-konstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
835	2-Oxy-4-Nitrophenyl-Phosphonsäure: 					
	pK_1 1,22 pK_2 5,39 $pK_3 > 12$	fehlt	$I \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
836	2-Methoxy-4-Nitrophenyl-Phosphonsäure: 					
	pK_1 1,53 pK_2 6,96	fehlt	$I \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1
837	2-Methoxy-4-Aminophenyl-Phosphonsäure: 					
	pK_2 8,22	fehlt	$I \simeq 0{,}1$	**E3b** **D1**	unsicher.	J1

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(c) Phosphinsäuren

838 Methyl-Phosphinsäure: $CH_3 \cdot PO_2H_2$

pK^- 3,08	25	$c = 0{,}01$	**E3b**	unsicher.	C28

839 Äthyl-Phosphinsäure: $CH_3 \cdot CH_2 \cdot PO_2H_2$

pK^- 3,29	25	$c = 0{,}01$	**E3b**	unsicher.	C28

840 n-Propyl-Phosphinsäure: $CH_3 \cdot (CH_2)_2 \cdot PO_2H_2$

pK^- 3,46	25	$c = 0{,}01$	**E3b**	unsicher.	C28

841 iso-Propyl-Phosphinsäure: $(CH_3)_2CH \cdot PO_2H_2$

pK^- 3,56	25	$c = 0{,}01$	**E3b**	unsicher.	C28

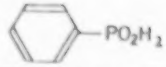
842 n-Butyl-Phosphinsäure: $CH_3 \cdot (CH_2)_3 \cdot PO_2H_2$

pK^- 3,41	25	$c = 0{,}01$	**E3b**	unsicher.	C28

843 tert.-Butyl-Phosphinsäure: $(CH_3)_3C \cdot PO_2H_2$

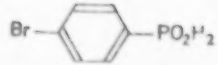
pK^- 4,24	25	$c = 0{,}01$	**E3b**	unsicher.	C28

844 Phenyl-Phosphinsäure:



pK^- 2,1	17	$c = 0{,}02$	**E3b**	unsicher.	L16

845 *p*-Bromphenyl-Phosphinsäure: L16



pK^- 2,1	17	$c = 0{,}02$	**E3b**	unsicher.	

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
846	*p*-Methoxyphenyl-Phosphinsäure:					
	pK 2,35	17	$c = 0{,}02$	**E3b**	unsicher.	L16
847	*p*-Dimethylaminophenyl-Phosphinsäure:					
	pK_1 2,1 pK_2 4,1	17	$c = 0{,}02$	**E3b**	unsicher.	L16
			43			
	Arsonsäuren					
848	Methyl-Arsonsäure: $CH_3{\cdot}AsO_3H_2$					
	K_1 $2{,}46 \cdot 10^{-4}$ K_2 $6{,}59 \cdot 10^{-9}$	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3
849	Kakodylsäure: $(CH_3)_2{\cdot}AsO_2H$					
	$5{,}33 \cdot 10^{-7}$	25	$\mathcal{J} = 0{,}03$	**E2b** u. **Kat.**	rel. zuv.	K11a
	$5{,}39 \cdot 10^{-7}$	25	$\mathcal{J} = 0{,}03$	**O2**	rel. zuv.	K11a
850	Äthyl-Arsonsäure: $CH_3{\cdot}CH_2{\cdot}AsO_3H_2$					
	K_1 $1{,}28 \cdot 10^{-4}$ K_2 $4{,}47 \cdot 10^{-9}$	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3

851 n-Propyl-Arsonsäure: $CH_3{\cdot}(CH_2)_2{\cdot}AsO_3H_2$

K_1 0,611·10^{-4} K_2 0,808·10^{-9}	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3

852 n-Butyl-Arsonsäure: $CH_3{\cdot}(CH_2)_3{\cdot}AsO_3H_2$

K_1 0,587·10^{-4} K_2 1,22·10^{-9}	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3

853 n-Pentyl-Arsonsäure: $CH_3{\cdot}(CH_2)_4{\cdot}AsO_3H_2$

K_1 0,723·10^{-4} K_2 0,859·10^{-9}	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3

854 n-Hexyl-Arsonsäure: $CH_3{\cdot}(CH_2)_5{\cdot}AsO_3H_2$

K_1 0,693·10^{-4} K_2 0,642·10^{-9}	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3

855 2-Chloräthyl-Arsonsäure: $CH_2Cl{\cdot}CH_2{\cdot}AsO_3H_2$

K_1 2,08·10^{-4} K_2 4,23·10^{-9}	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3

856 2-Chlor-n-propyl-Arsonsäure: $CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}AsO_3H_2$

K_1 1,73·10^{-4} K_2 4,05·10^{-9}	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3

857 3-Chlor-n-propyl-Arsonsäure: $CH_2Cl{\cdot}(CH_2)_2{\cdot}AsO_3H_2$

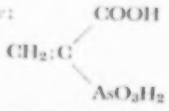
K_1 2,36·10^{-4} K_2 2,96·10^{-9}	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3

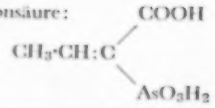
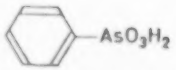
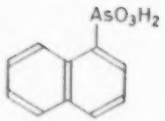
858 3-Chlor-n-butyl-1-Arsonsäure: $CH_3{\cdot}CHCl{\cdot}(CH_2)_2{\cdot}AsO_3H_2$

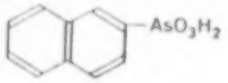
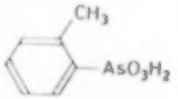
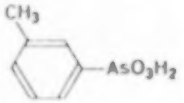
K_1 1,13·10^{-4} K_2 1,43·10^{-9}	18	$\mathcal{J} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3

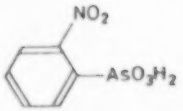
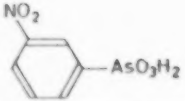
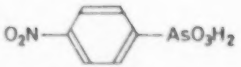
Bezeichnung 43-43

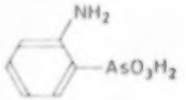
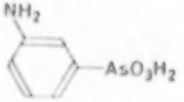
No. 859–868

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
859	3-Chlor-n-pentyl-1-Arsonsäure: $CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}(CH_2)_2{\cdot}AsO_3H_2$					
	K_1 1,93·10^{-4} K_2 1,71·10^{-9}	18	$\bar{\gamma} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3
860	3-Chlor-n-hexyl-1-Arsonsäure: $CH_3{\cdot}(CH_2)_2{\cdot}CHCl{\cdot}(CH_2)_2{\cdot}AsO_3H_2$					
	K_1 3,06·10^{-4} K_2 4,33·10^{-9}	18	$\bar{\gamma} \simeq 0{,}02$	**E3b** **D1**	unsicher.	B3
861	Arsonessigsäure: $COOH{\cdot}CH_2{\cdot}AsO_3H_2$					
	K_1 1,16·10^{-3} K_2 2,14·10^{-5} K_3 2,1·10^{-8}	25	$c = 0{,}003$	**E3b**	unsicher.	B4
862	Arsonbuttersäure: $COOH{\cdot}(CH_2)_3{\cdot}AsO_3H_2$					
	K_1 0,98·10^{-3} K_2 1,20·10^{-5} K_3 2,3·10^{-8}	25	$c = 0{,}003$	**E3b**	unsicher.	B4
863	Arsonvaleriansäure: $COOH{\cdot}(CH_2)_4{\cdot}AsO_3H_2$					
	K_1 1,01·10^{-3} K_2 1,29·10^{-5} K_3 1,8·10^{-8}	25	$c = 0{,}003$	**E3b**	unsicher.	B4
864	α-Arsonacrylsäure: 					

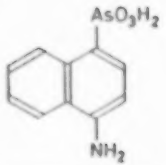
	K_1 1,23·10^{-3} K_2 5,95·10^{-6} K_3 2,49·10^{-9}	fehlt	$\epsilon = 0{,}007$	**E3b** **D1**	unsicher.	B5
865	α-Arsoncrotonsäure: 					
	K_1 4,37·10^{-4} K_2 2,48·10^{-5} K_3 1,77·10^{-9}	fehlt	$\epsilon = 0{,}005$	**E3b** **D1**	unsicher.	B5
866	β-Arsoncrotonsäure: $COOH{\cdot}CH{:}C(CH_3){\cdot}AsO_3H_2$					
	K_1 2,58·10^{-3} K_2 9,42·10^{-6} K_3 1,56·10^{-9}	fehlt	$\epsilon = 0{,}0065$	**E3b** **D1**	unsicher.	B5
867	Phenyl-Arsonsäure: 					
	K_1 2,6·10^{-4}			**E3**	unsicher. Keine näheren Angaben.	B48
	K_1 3,4·10^{-4} K_2 3,3·10^{-9}	22		**E3b**	unsicher. K_c-Werte.	P12
868	α-Naphthyl-Arsonsäure: 					
	K_1 2,2·10^{-4} K_2 2,2·10^{-9}	22		**E3b**	unsicher. K_c-Werte.	P12

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
869	*β*-Naphthyl-Arsonsäure: 					
	K_2 3,4-10 ^{9}	22		**E3b**	unsicher. K_c-Werte.	P12
870	*o*-Tolyl-Arsonsäure: 					
	K_1 1,5-10 ^{4} K_2 1,4-10 ^{9}	22		**E3b**	unsicher. K_c-Werte.	P12
871	*m*-Tolyl-Arsonsäure: 					
	K_1 1,5-10 ^{4} K_2 2,5-10 ^{9}	22		**E3b**	unsicher. K_c-Werte.	P12
872	*p*-Tolyl-Arsonsäure:					

	K_1 2,0·10^{-4} K_2 2,1·10^{-9}	22	**E3b**	unsicher. K_c-Werte.	P12
	K_1 1,7·10^{-4}	18	**E3**	unsicher. Ohne nähere Angaben.	B48
	K_1 1,86·10^{-4}			unsicher. Ohne nähere Angaben.	E7a
873	*o*-Nitrophenyl-Arsonsäure: 				
	K_1 4,3·10^{-4} K_2 2,9·10^{-9}	22	**E3b**	unsicher. K_c-Werte.	P12
874	*m*-Nitrophenyl-Arsonsäure: 				
	K_1 3,9·10^{-4} K_2 15,9·10^{-9}	22	**E3b**	unsicher. K_c-Werte.	P12
875	*p*-Nitrophenyl-Arsonsäure: 				
	K_1 12,7·10^{-4} K_2 15,9·10^{-9}	22	**E3b**	unsicher. K_c-Werte.	P12
	K_1 8,3·10^{-4}		**E3**	unsicher. Ohne nähere Angaben.	B48
	K_1 9,09·10^{-4}			unsicher. Ohne nähere Angaben.	E7a

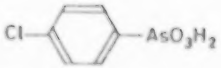
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
876	*o*-Aminophenyl-Arsonsäure: 					
	K_2 1,7·10⁻⁴ K_3 2,2·10⁻⁹	22		**E3b**	unsicher. K_c-Werte.	P12
877	*m*-Aminophenyl-Arsonsäure: 					
	K_2 0,9·10⁻⁴ K_3 2,4·10⁻⁹	22			unsicher. K_c-Werte.	P12
878	*p*-Aminophenyl-Arsonsäure:					
	K_2 0,9·10⁻⁴ K_3 1,2·10⁻⁹	22		**E3b**	unsicher. K_c-Werte.	P12
	K_2 4,4·10⁻⁵			**E3**	unsicher. Ohne nähere Angaben.	B48
	K_2 1,0·10⁻⁴				unsicher. Ohne nähere Angaben.	E7a

879 4-Aminonaphthyl-1-Arsonsäure:



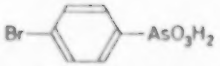
K_3 $0{,}67 \cdot 10^{-9}$	22	**E3b**	unsicher. K_c-Werte.	P12

880 *p*-Chlorphenyl-Arsonsäure:



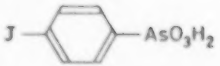
K_1 $4{,}7 \cdot 10^{-4}$ K_2 $5{,}6 \cdot 10^{-4}$	22	**E3b**	unsicher. K_c-Werte.	P12
K_1 $3{,}15 \cdot 10^{-4}$			unsicher. Ohne nähere Angaben.	E7a

881 *p*-Bromphenyl-Arsonsäure:

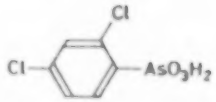
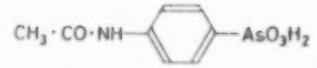


K_1 $5{,}6 \cdot 10^{-4}$ K_2 $6{,}5 \cdot 10^{-9}$	22	**E3b**	unsicher. K_c-Werte.	P12

882 *p*-Jodphenyl-Arsonsäure:



K_2 $5{,}7 \cdot 10^{-9}$	22	**E3b**	unsicher. K_c-Werte.	P12

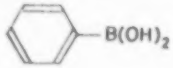
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
883	Benzoesäure-4-Arsonsäure:					
	K_1 $14{,}0 \cdot 10^{-4}$ K_{carboxyl} $6{,}0 \cdot 10^{-5}$ K_2 $2{,}6 \cdot 10^{-9}$	22		**E3b**	unsicher. K_c-Werte.	P12
884	*p*-Oxyphenyl-Arsonsäure:					
	K_1 $1{,}3 \cdot 10^{-4}$ $K_{\text{(phenol)}}$ $4{,}3 \cdot 10^{-9}$ K_2 $9{,}0 \cdot 10^{-11}$	22		**E3b**	unsicher. K_c-Werte.	P12
	K_1 $8{,}7 \cdot 10^{-5}$			**E3**	unsicher. Ohne nähere Angaben.	B48
885	2,4-Dichlorphenyl-Arsonsäure: 					
	K_1 $7{,}2 \cdot 10^{-4}$			**E3**	unsicher. Ohne nähere Angaben.	B48
886	*p*-Acetylaminophenyl-Arsonsäure: 					
	K_1 $1{,}9 \cdot 10^{-4}$			**E3**	unsicher. Ohne nähere Angaben.	B48

887 *p*-Methoxyphenyl-Arsonsäure:

K_1 9,1·10^{-4}			**E3**	unsicher. Ohne nähere Angaben.	B48

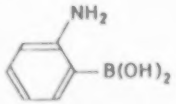
44

888 Phenyl-Borsäure:



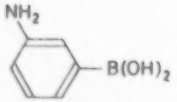
13,7·10^{-10}		$\mathcal{J}$ = 0,005 bis 0,03	**E3a** **D1**	rel. zuv.	B47

889 *o*-Aminophenyl-Borsäure:

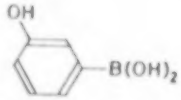
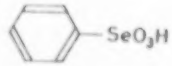
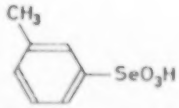


K_1 2,7·10^{-5} K_2 5,9·10^{-10}	25	$\mathcal{J} \leq$ 0,08	**E3a** **D1**	unsicher.	C18

890 *m*-Aminophenyl-Borsäure:



K_1 3,5·10^{-5} K_2 15,4·10^{-10}	25	$\mathcal{J} \leq$ 0,08	**E3a** **D1**	unsicher.	C18

No.	*Name, Formel u. Dissoziations-konstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
891	*p*-Aminophenyl-Borsäure:					
	K_1 $19{,}5 \cdot 10^{-5}$ K_2 $6{,}7 \cdot 10^{-10}$	25	$J \leq 0{,}08$	**E3a** **D1**	unsicher.	C18
892	*m*-Oxyphenyl-Borsäure: 					
	K_1 $2{,}79 \cdot 10^{-9}$ K_2 $1{,}44 \cdot 10^{-11}$	25	$J \leq 0{,}08$	**E3a** **D1**	unsicher.	C18
893	Phenyl-Selenonsäure: 					
	pK 4,79	25		**E3b**	unsicher.	M2
894	*m*-Tolyl-Selenonsäure: 					
	pK 4,80	25		**E3b**	unsicher.	M2

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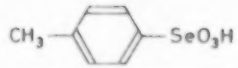
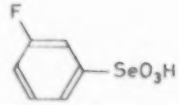
895 *p*-Tolyl-Selenonsäure:



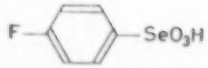
p*K* 4,88	25	**E3b**	unsicher.	M2

896 *m*-Fluorphenyl-Selenonsäure:



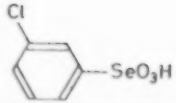
p*K* 4,34	25	**E3b**	unsicher.	M2

897 *p*-Fluorphenyl-Selenonsäure:



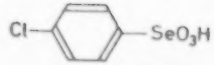
p*K* 4,50	25	**E3b**	unsicher.	M2

898 *m*-Chlorphenyl-Selenonsäure:

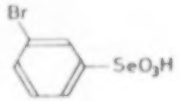
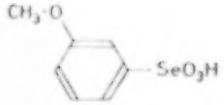


p*K* 4,47	25	**E3b**	unsicher.	M2

899 *p*-Chlorphenyl-Selenonsäure:



p*K* 4,48	25	**E3b**	unsicher.	M2

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
900	*m*-Bromphenyl-Selenonsäure: 					
	p*K* 4,43	25		**E3b**	unsicher.	**M2**
901	*p*-Bromphenyl-Selenonsäure:					
	p*K* 4,50	25		**E3b**	unsicher.	**M2**
902	*m*-Methoxyphenyl-Selenonsäure: 					
	p*K* 4,65	25		**E3b**	unsicher.	**M2**
903	*p*-Methoxyphenyl-Selenonsäure:					
	p*K* 5,05	25		**E3b**	unsicher.	**M2**

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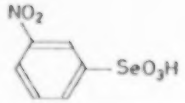
904 *m*-Nitrophenyl-Selenonsäure:

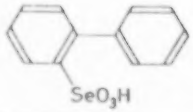


pK 4,07	25	**E3b**	unsicher.	M2

905 *p*-Nitrophenyl-Selenonsäure:

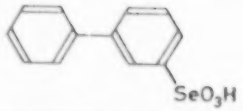
pK 4,00	$\mathcal{J} = 0{,}003$	**E3a**	unsicher.	G16

906 2-Biphenylyl-Selenonsäure:



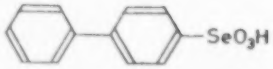
pK 4,67	25	**E3b**	unsicher.	M2

907 3-Biphenylyl-Selenonsäure:

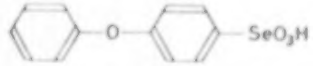
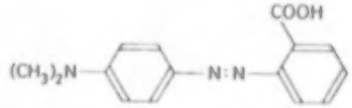
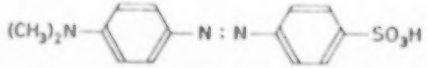


pK 4,87	$\mathcal{J} = 0{,}003$	**E3a**	unsicher.	G16

908 4-Biphenylyl-Selenonsäure:



pK 4,53	$\mathcal{J} = 0{,}003$	**E3a**	unsicher.	G16

No.	Name, Formel u. Dissoziationskonstante K	T (°C)	Bemerkungen	Methode	Kritik	Lit.
909	*p*-Phenoxyphenyl-Selenonsäure: 					
	pK 4,88		$\mathcal{I} = 0{,}003$	**E3a**	unsicher.	G16
			51			
	Indikatoren					
	(a) Azofarbstoffe					
910	Methylrot: 					
	K_1 2,32·10 $^{-3}$ K_2 1,44·10 $^{-5}$	28	$\mathcal{I} = 0{,}25$ bis 1,8	**O5**	rel. zuv.	M18
	K_2 1,04·10 $^{-5}$	22			unsicher. K_c-Werte.	C14
911	Methylorange: 					
	K_2 3,03·10 $^{-4}$	18	$c = 0{,}0004$ bis 0,02	**O1**	rel. zuv.	S20
	pK_2 3,37	28	$\mathcal{I} = 0{,}25$ bis 1,8	**O5**	rel. zuv.	M18

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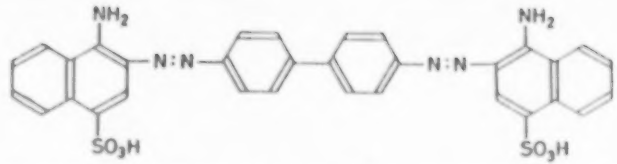
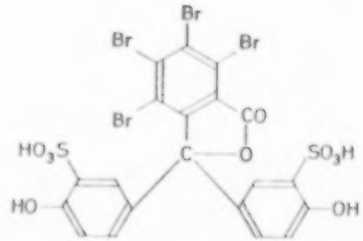
912 Kongorot:



K_2 6,46·10^{-5}	28	$\mathcal{J}$ = 0,25 bis 1,8	**O5**	rel. zuv.	M18

(*b*) *Phthaleine*

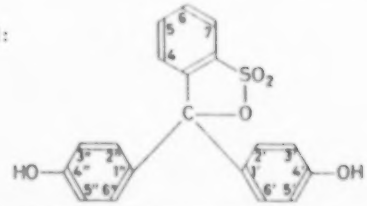
913 Phenol-Tetrabrom-Phthalein-Disulfonsäure:



pK_2 8,660	25	$\mathcal{J}$ = 0,02 bis 2	**O5**	rel. zuv.	M19

(*c*) *Sulfophthaleine*

Allgemeine Formel:



Bezeichnung 51–52

No. 914–925

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
914	Phenolrot (Phenolsulfophthalein)					
	p*K* 8,08	20	$\mathcal{J} = 0{,}015$ bis 0,25	**O5**	unsicher.	S15
915	Chlorphenolblau (5′,5″-Dichlor)					
	$3{,}7 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}002$ bis 0,06	**O5**	unsicher.	P1
916	Chlorphenolrot (3′,3″-Dichlor)					
	$11{,}0 \cdot 10^{-7}$	25			unsicher. K_2-Werte.	C14
917	Bromphenolblau (3′,5′,3″,5″-Tetrabrom)					
	$5{,}835 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}003$ bis 0,03	**O2**	rel. zuv.	M21
918	Jodphenolblau (3′,5′,3″,5″-Tetrajod)					
	$6{,}4 \cdot 10^{-3}$	25	$\mathcal{J} = 0{,}002$ bis 0,06	**O5**	unsicher.	P1
919	*m*-Kresolpurpur (2′,2″-Dimethyl)					
	$2{,}12 \cdot 10^{-2}$	25	$\mathcal{J} = 0{,}003$ bis 0,03	**O2**	rel. zuv.	M21
	p*K* 1,703	25	$\mathcal{J} = 0{,}001$ bis 2	**O5** **D1**	zuv.	S2
920	Bromkresolgrün (2′,2″-Dimethyl-3′,5′,3″,5″-Tetrabrom)					
	p*K* 4,92	20	$\mathcal{J} = 0{,}015$ bis 0,25	**O5**	rel. zuv.	S15

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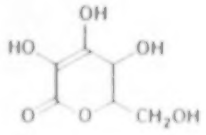
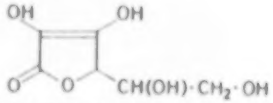
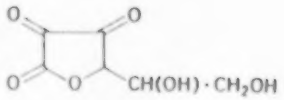
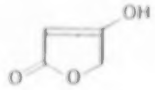
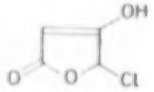
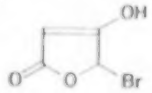
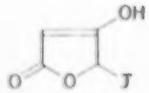
	$1{,}069 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}003$ bis $0{,}03$	**O2**	rel. zuv.	M21
	$1{,}11 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}0008$ bis $0{,}027$	**O4**	rel. zuv.	K4
	$1{,}03 \cdot 10^{-5}$	25	$\mathcal{J} = 0{,}01$ bis $0{,}2$	**O5**	rel. zuv.	G24
					Weitere Messungen: K_c-Werte G14.	
921	Bromkresolpurpur (5′,5″-Dibrom-3′,3″-Dimethyl)					
	pK_2 6,33	28	$\mathcal{J} = 0{,}25$ bis 2	**O5**	rel. zuv.	M18
	pK_2 6,46	20	$\mathcal{J} = 0{,}015$ bis $0{,}2$	**O5**	rel. zuv.	S15
922	Bromthymolblau (2′,2″-Dimethyl-3′,3″-Dibrom-5′,5″-Di-iso-propyl)					
	pK 7,341	23	$\mathcal{J} = 0{,}02$ bis 2	**O5**	rel. zuv.	M19
	$3{,}58 \cdot 10^{-8}$	25	$\mathcal{J} = 0{,}01$ bis $0{,}2$	**O5**	rel. zuv.	G24
			52			
	(*a*) *Acide—OH-Gruppen* (*ausgenommen Phenole*)					
923	Redukton: CH(OH) : C(OH)·CHO					
	$1{,}17 \cdot 10^{-5}$	20	$c = 0{,}01$	**E3a**	unsicher.	C3
924	Mesoxal-Dialdehyd: $CHO \cdot C(OH)_2 \cdot CHO$					
	K_1 2 $\cdot 10^{-4}$ K_2 $2{,}5 \cdot 10^{-4}$			**E3**	unsicher. K_c-Werte; langsame Gleichgewichtseinstellung.	C3
925	Reduktinsäure: $CH_2 \cdot CH_2 \cdot COH$: COH·CO					
	$1{,}9 \cdot 10^{-5}$	20	$c = 0{,}02$	**E3b** **D1**	unsicher.	C5

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
926	Gluco-ascorbinsäure: 					
	K_1 (a) $5{,}5 \cdot 10^{-5}$ (b) $7{,}1 \cdot 10^{-5}$ K_2 (a) $2{,}6 \cdot 10^{-12}$ (b) $5{,}6 \cdot 10^{-13}$			(a) **E3b** (b) **O2**	unsicher. K_c-Werte.	C6
927	Ascorbinsäure: 					
	K_1 $2 \cdot 10^{-5}$ K_2 $6{,}3 \cdot 10^{-13}$	10		**E3b**	unsicher. Keine näheren Angaben.	C4
	K_1 $6{,}76 \cdot 10^{-5}$ K_2 $2{,}75 \cdot 10^{-12}$	20				
	pK_1 4,15 pK_2 11,50	17,5 18		**E3b** **D1**	unsicher. Mikromethode.	B37
	K_1 $5{,}06 \cdot 10^{-5}$			**L**	unsicher. Ohne nähere Angaben.	S9
	K_1 $7{,}59 \cdot 10^{-5}$ K_2 $3{,}09 \cdot 10^{-12}$			**E3b** **D1**	unsicher. Keine experimentellen Angaben.	K45
	K_1 $6{,}17 \cdot 10^{-5}$	30	$\mathcal{J} = 0{,}001$ bis $0{,}2$	**E3a** **D1**	rel. zuv.	B7

	K_1 $6{,}3 \cdot 10^{-5}$ K_2 $2{,}7 \cdot 10^{-12}$	29	$\mathcal{J} = 0{,}006$ bis $0{,}05$	**L1** **E3a**	unsicher. Keine experimentellen Angaben. K_c-Werte.	G13
928	Dehydroascorbinsäure: 					
	K_1 $6 \cdot 10^{-4}$ K_2 $1{,}2 \cdot 10^{-8}$ K_3 $5{,}1 \cdot 10^{-11}$	20		**E3b**	unsicher. Keine näheren Angaben.	C4
	pK_2 9,0	35		**O1**	unsicher. Keine experimentellen Angaben.	B12
929	Glucose: $CH_2(OH) \cdot [CH(OH)]_4 \cdot CHO$					
	pK 12,92 12,43	0 18	$\mathcal{J} = 0{,}07$ bis $0{,}25$	**E** **D1**	unsicher. Besondere Methode.	T4
930	Mannose: $CH_2(OH) \cdot [CH(OH)]_4 \cdot CHO$.					
	pK 14,09 13,50	0 18	$\mathcal{J} = 0{,}07$ bis $0{,}25$	**E** **D1**	unsicher. Besondere Methode.	T4
931	Sorbose: $CH_2(OH) \cdot [CH(OH)]_3 \cdot CO \cdot CH_2 \cdot OH$					
	pK 14,14 13,57	0 18	$\mathcal{J} = 0{,}07$ bis $0{,}25$	**E** **D1**	unsicher. Besondere Methode.	T4
932	2,2,2-Trinitro-Äthanol: $(NO_2)_3C \cdot CH_2 \cdot OH$					
	$4{,}3 \cdot 10^{-3}$			**E3**	unsicher. Nähere Angaben fehlen: alkalisch zersetzlich.	M9

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
933	Tetronsäure: 					
	pK 3,76	25		**E3a**	rel. zuv.	K43
934	α-Chlor-Tetronsäure: 					
	pK 2,13	25		**E3a**	rel. zuv.	K43
935	α-Brom-Tetronsäure: 					
	pK 2,23	25		**E3a**	rel. zuv.	K43
936	α-Jod-Tetronsäure: 					
	pK 2,31	25		**E3a**	rel. zuv.	K43

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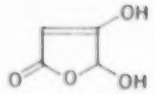
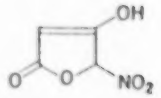
937 α-Oxy-Tetronsäure:



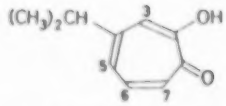
pK 4,37	25	**E3a**	rel. zuv.	K43

938 α-Nitro-Tetronsäure:



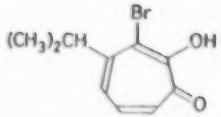
pK 1,68	25 $\mathcal{J} = 0{,}008$	**E3a**	unsicher.	K44

939 Hinokiol:

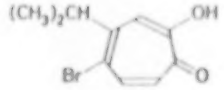
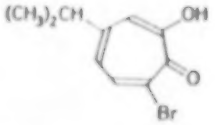
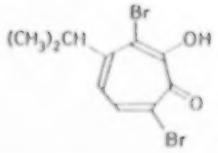


$6{,}2 \cdot 10^{-8}$		**E3b**	unsicher.	N10

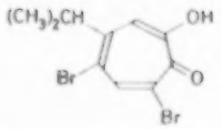
940 3-Brom-Hinokiol:



$2{,}1 \cdot 10^{-5}$		**E3b**	unsicher.	N10

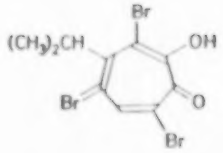
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
941	5-Brom-Hinokiol: 					
	$2{,}9 \cdot 10^{-5}$			**E3b**	unsicher.	N10
942	7-Brom-Hinokiol: 					
	$5{,}2 \cdot 10^{-5}$			**E3b**	unsicher.	N10
943	3,7-Dibrom-Hinokiol: 					
	$3{,}6 \cdot 10^{-5}$			**E3b**	unsicher.	N10

944 5,7-Dibrom-Hinokiol:



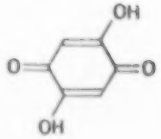
$5{,}2 \cdot 10^{-5}$	**E3b**	unsicher.	N10

945 3,5,7-Tribrom-Hinokiol:

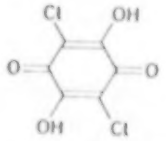
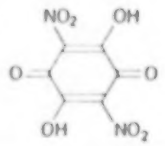
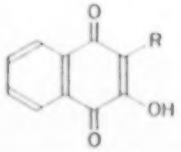


$1{,}0 \cdot 10^{-5}$	**E3b**	unsicher.	N10

946 2,5-Dioxy-Benzochinon:



pK_1 2,71 pK_2 5,18	**O5**	unsicher. K_c-Werte; ohne experimentelle Angaben.	S14a

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
947	Chloranilsäure: 					
	K_1 $8{,}2 \cdot 10^{-2}$ K_2 $3{,}8 \cdot 10^{-3}$			**O5**	unsicher. K_c-Werte; ohne experimentelle Angaben.	T3
	pK_1 0,58 pK_2 3,18			**O5**	unsicher. K_c-Werte; ohne experimentelle Angaben.	S14a
948	2,5-Dioxy-3,6-Dinitro-Benzochinon: 					
	pK_1 −3,0 pK_2 −0,5				unsicher. K_c-Werte.	S14a
	2-Oxy-3-R-Naphthochinone-1,4: 					

949 R = H

pK 4,00	26–33	$\mathcal{J}$ = 0,1 bis 0,2	**O5**	unsicher. EB

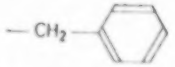
950 R = $-(CH_2)_2{\cdot}CH(CH_3)_2$

pK 5,13	26–33	$\mathcal{J}$ = 0,1 bis 0,2	**O5**	unsicher. EB

951 R = $-CH_2{\cdot}CH(OH){\cdot}CH(CH_3)_2$

pK 4,96	26–33	$\mathcal{J}$ = 0,1 bis 0,2	**O5**	unsicher. EB

952 R = Benzyl:



pK 4,9	26–33	$\mathcal{J}$ = 0,1 bis 0,2	**O5**	unsicher. EB

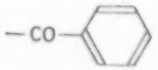
953 R = $-CH_2{\cdot}CO{\cdot}CH_3$

pK 4,12	26–33	$\mathcal{J}$ = 0,1 bis 0,2	**O5**	unsicher. EB

954 R = $-CH_2{\cdot}N(CH_3)_2$

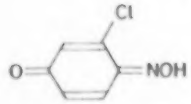
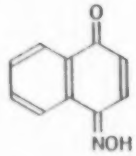
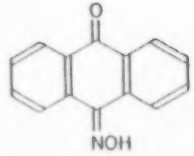
pK 2,32	26–33	$\mathcal{J}$ = 0,1 bis 0,2	**O5**	unsicher. EB

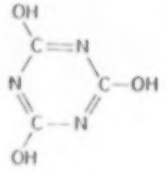
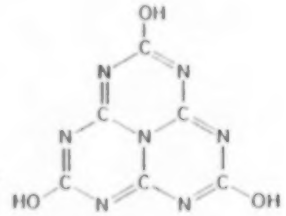
955 R = Benzoyl:



pK 2,17	26–33	$\mathcal{J}$ = 0,1 bis 0,2	**O5**	unsicher. EB

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
956	R = Phenyl:					
	pK 4,35	26–33	$\mathcal{I}$ = 0,1 bis 0,2	**O5**	unsicher.	E8
957	R = —CH:CH·CH$_3$					
	pK 4,8	26–33	$\mathcal{I}$ = 0,1 bis 0,2	**O5**	unsicher.	E8
958	Acetoxim: $(CH_3)_2C{:}NOH$					
	$3{,}83 \cdot 10^{-13}$	25	$\mathcal{I}$ = 0,04 bis 0,22	**Kat.**	unsicher.	K16
959	Methyl-Äthyl-Ketoxim: $CH_3{\cdot}CH_2{\cdot}C(CH_3){:}NOH$					
	$3{,}54 \cdot 10^{-13}$	25	$\mathcal{I}$ = 0,04 bis 0,22	**Kat.**	unsicher.	K16
960	Diäthyl-Ketoxim: $(CH_3{\cdot}CH_2)_2C{:}NOH$					
	$2{,}54 \cdot 10^{-13}$	25	$\mathcal{I}$ = 0,04 bis 0,22	**Kat.**	unsicher.	K16
961	Benzochinon-Monoxim:					

	pK (a) 6,21 (b) 6,2 (c) 6,4		$\mathcal{J} = 0{,}01$	(a) **O5** (b) **E3a, D1** (c) **L2**	rel. zuv. bis unsicher. Wenig experimentelle Angaben. H28
962	3-Chlor-Benzochinon-4-Monoxim: 				
	pK 5,68	fehlt	$\mathcal{J} \simeq 0{,}01$	**O5**	rel. zuv. bis unsicher. Wenig experimentelle Angaben. H28
963	1,4-Naphthochinon-Monoxim: 				
	pK 8,01			**O5**	rel. zuv. bis unsicher. Wenig experimentelle Angaben. H28
964	9,10-Anthrachinon-Monoxim: 				
	pK 9,78			**O5**	rel. zuv. bis unsicher. Wenig experimentelle Angaben. H28

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
965	Cyanursäure: 					
	K_1 1,65·10 $^{-7}$			**E3b** **D1**	unsicher.	R5
966	Cyanchursäure: 					
	K_1 1,0·10 $^{-3}$ K_2 6,3·10 $^{-7}$ K_3 1,12·10 $^{-9}$			**E3b** **D1**	unsicher.	R5

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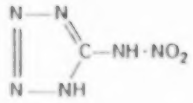
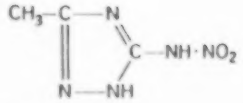
(*b*) *Acide NH-Gruppen.*

967 5-Nitroamino-Tetrazol:



K_1 sehr stark. K_2 $9 \cdot 10^{-7}$		**E3b**	unsicher.	L19

968 3-Methyl-5-Nitroamino-1,2,4-Triazol:



K_1 $1{,}6 \cdot 10^{-5}$		**E3b**	unsicher.	L19

Weitere Messungen an Tetrazolderivaten: V6; M20b.

969 Methylen-Dinitroamin: $NO_2 \cdot NH \cdot CH_2 \cdot NH \cdot NO_2$

pK_1 5,0 pK_2 6,6	$\mathcal{J} \simeq 0{,}003$	**E3a**	unsicher.	L20

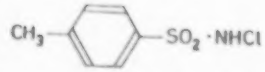
970 Äthylen-Dinitroamin: $NO_2 \cdot NH \cdot (CH_2)_2 \cdot NH \cdot NO_2$

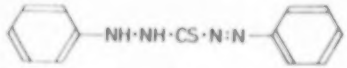
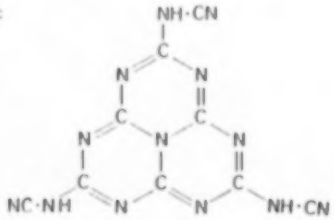
pK_1 5,35 pK_2 6,66	$\mathcal{J} = 0{,}003$	**E3a**	unsicher.	L20

971 Trimethylen-Dinitroamin: $NO_2 \cdot NH \cdot (CH_2)_3 \cdot NH \cdot NO_2$

pK_1 5,59 pK_2 6,85	$\mathcal{J} = 0{,}003$	**E3a**	unsicher.	L20

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
972	Tetramethylen-Dinitroamin: $NO_2{\cdot}NH{\cdot}(CH_2)_4{\cdot}NH{\cdot}NO_2$					
	pK_1 5,87 pK_2 6,98		$\bar{f}$ = 0,003	**E3a**	unsicher.	L20
	Nitroguanyl-Hydrazone (Nitro-Amino-Guanidin-Hydrazone): $NO_2{\cdot}N{:}\,C(NH_2){\cdot}NH{\cdot}N{:}\,R$					
973	R : O = Aceton					
	pK 8,60			**O5**	unsicher. Ohne nähere Angaben.	H34
974	R : O = Cyclohexanon					
	pK 8,80			**O5**	unsicher. Ohne nähere Angaben.	H34
975	R : O = Phenyl-Acetaldehyd					
	pK 8,50			**O5**	unsicher. Ohne nähere Angaben.	H34
976	R : O = Zimtaldehyd					
	pK 8,28			**O5**	unsicher. Ohne nähere Angaben.	H34
977	R : O = Benzaldehyd					
	pK 8,38			**O5**	unsicher. Ohne nähere Angaben.	H34

978	R:O = 2-Oxy-Benzaldehyd			
	pK 8,50	**O5**	unsicher. Ohne nähere Angaben.	H34
979	R:O = 2-Methoxy-Benzaldehyd			
	pK 8,70	**O5**	unsicher. Ohne nähere Angaben.	H34
980	R:O = 4-Methoxy-Benzaldehyd			
	pK 8,83	**O5**	unsicher. Ohne nähere Angaben.	H34
981	R:O = 4-Methyl-Benzaldehyd			
	pK 8,80	**O5**	unsicher. Ohne nähere Angaben.	H34
982	R:O = 4-iso-Propyl-Benzaldehyd			
	pK 8,90	**O5**	unsicher. Ohne nähere Angaben.	H34
983	R:O = 4-Dimethylamino-Benzaldehyd			
	pK 9,2	**O5**	unsicher. Ohne nähere Angaben.	H34
			Weitere Messungen an Nitro-Guanidin und Derivaten: V6.	
984	*N*-Chlor-*p*-Tolyl-Sulfonamid: 			
	$2{,}8 \cdot 10^{-5}$	J = 0,01 bis 0,08	**E3b** unsicher.	M26

No.	*Name, Formel u. Dissoziations-konstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
985	Diphenyl-Thiocarbazon: 					
	$1{,}5 \cdot 10^{-5}$			Vertlgs. Gleichgew.	unsicher. Sehr schwer löslich.	S3
986	Hydromelonsäure: 					
	K_1 sehr gross K_2 $3{,}2 \cdot 10^{-3}$ K_3 $1{,}26 \cdot 10^{-5}$			**E3b** **D1**	unsicher.	R5
	(*c*) *Acide CH-Gruppen*					
987	α-Jod-Acetessigsäure-Äthylester: $CH_3 \cdot CO \cdot CHJ \cdot CO \cdot O \cdot CH_2 \cdot CH_3$					
	p*K* 7,0	25		**E3a**	unsicher.	K43
988	*p*-Nitrobenzyl-Cyanid:					

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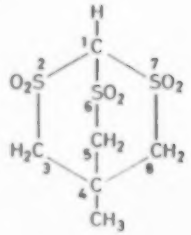
	$4 \cdot 10^{-14}$	25	**O4**	unsicher.	S30

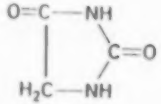
989 4-Methyl-2,6,7-Trithiabicyclo[2,2,2]Octan-2,2,6,6,7,7-Hexaoxyd:



	pK 3,30		**E3b**	unsicher.	D21

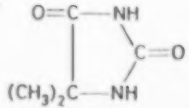
(d) Acides H an heterocyclischen Ringen

990 Hydantoin:

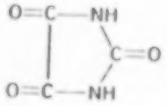
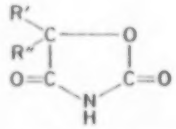


	pK 9,12	24	$\mathcal{J} = 0{,}01$ bis $0{,}03$	**E3a** unsicher.	Z1a

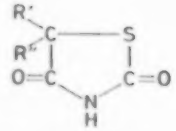
991 5,5-Dimethyl-Hydantoin:



	pK 9,19	24	$\mathcal{J} = 0{,}01$ bis $0{,}03$	**E3a** unsicher.	Z1a

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
992	Parabansäure: 					
	pK 6,10		$\mathcal{J} = 0{,}1$	**E2b**	unsicher. Keine näheren Angaben; Salz hydrolisiert leicht.	A9
	2,4-Dioxo-Oxazolidin-Derivate: 					
993	$R' = R'' = -CH_3$					
	$7{,}79 \cdot 10^{-7}$			**E3b**	unsicher. K_c-Werte.	E6 E7
994	$R' = -CH_3$; $R'' = -CH_2 \cdot CH_3$					
	$1{,}27 \cdot 10^{-6}$			**E3b**	unsicher. K_c-Werte.	E6 E7
995	$R' = R'' = -CH_2 \cdot CH_3$					
	$1{,}98 \cdot 10^{-6}$			**E3b**	unsicher. K_c-Werte.	E6 E7

2,4-Dioxo-Thiazolidin-Derivate:



996 $R' = R'' =$ —CH_3

$2{,}30 \cdot 10^{-7}$ — **E3b** unsicher. K_c-Werte. — E6 E7

997 $R' = R'' =$ —$CH_2 \cdot CH_3$

$3{,}84 \cdot 10^{-7}$ — **E3b** unsicher. K_c-Werte. — E6 E7

998 $R' = R'' =$ —$CH_2 \cdot CH_2 \cdot CH_3$

$4{,}30 \cdot 10^{-7}$ — **E3b** unsicher. K_c-Werte. — E6 E7

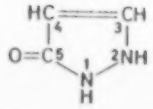
999 $R' = R'' =$ —$CH{:}CH \cdot CH_3$

$7{,}19 \cdot 10^{-7}$ — **E3b** unsicher. K_c-Werte. — E6 E7

Weitere Messungen: R4.

5-Pyrazolon-Derivate;

Allgemeine Formel:

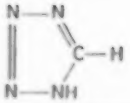


No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
1000	3-Phenyl-5-Pyrazolon					
	pK 7,4			**E3b**	unsicher.	Gla
1001	3-Phenyl-4-Methyl-5-Pyrazolon					
	pK 7,6			**E3b**	unsicher.	Gla
1002	3-Phenyl-4-Äthyl-5-Pyrazolon					
	pK 7,8			**E3b**	unsicher.	Gla
1003	3-Phenyl-4-n-Propyl-5-Pyrazolon					
	pK 8,0			**E3b**	unsicher.	Gla
1004	3-Phenyl-4-n-Butyl-5-Pyrazolon					
	pK 8,2			**E3b**	unsicher.	Gla
1005	3-Phenyl-4-n-Pentyl-5-Pyrazolon					
	pK 8,4			**E3b**	unsicher.	Gla
1006	3-Phenyl-4-n-Hexyl-5-Pyrazolon					
	pK 8,6			**E3b**	unsicher.	Gla
1007	3-Phenyl-4-n-Heptyl-5-Pyrazolon					
	pK 9,2			**E3b**	unsicher.	Gla

1008	3-Phenyl-4-n-Octyl-5-Pyrazolon			
	p*K* 10,2	**E3b**	unsicher.	Gla
1009	3-Phenyl-4-n-Nonyl-5-Pyrazolon			
	p*K* 10,6	**E3b**	unsicher.	Gla
1010	3-Phenyl-4-n-Decyl-5-Pyrazolon			
	p*K* 11,0	**E3b**	unsicher.	Gla
1011	3-Phenyl-4-Benzyl-5-Pyrazolon			
	p*K* 7,7	**E3b**	unsicher.	Gla
1012	1,3-Diphenyl-5-Pyrazolon			
	p*K* 6,2	**E3b**	unsicher.	Gla
1013	1,3-Diphenyl-4-Methyl-5-Pyrazolon			
	p*K* 7,8	**E3b**	unsicher.	Gla
1014	1,3-Diphenyl-4-Äthyl-5-Pyrazolon			
	p*K* 8,0	**E3b**	unsicher.	Gla
1015	1,3-Diphenyl-4-n-Propyl-5-Pyrazolon			
	p*K* 7,0	**E3b**	unsicher.	Gla
1016	1,3-Diphenyl-4-n-Butyl-5-Pyrazolon			
	p*K* 7,2	**E3b**	unsicher.	Gla

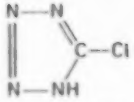
No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
1017	1,3-Diphenyl-4-n-Pentyl-5-Pyrazolon					
	pK 7,3			**E3b**	unsicher.	Gla
1018	1,3-Diphenyl-4-n-Hexyl-5-Pyrazolon					
	pK 7,4			**E3b**	unsicher.	Gla
1019	1,3-Diphenyl-4-n-Heptyl-5-Pyrazolon					
	pK 8,0			**E3b**	unsicher.	Gla
1020	1,3-Diphenyl-4-n-Octyl-5-Pyrazolon					
	pK 7,5			**E3b**	unsicher.	Gla
1021	1,3-Diphenyl-4-n-Nonyl-5-Pyrazolon					
	pK 7,2			**E3b**	unsicher.	Gla
1022	1,3-Diphenyl-4-n-Decyl-5-Pyrazolon					
	pK 6,7			**E3b**	unsicher.	Gla
1023	1,3-Diphenyl-4-Benzyl-5-Pyrazolon					
	pK 7,6			**E3b**	unsicher.	Gla

1024 Tetrazo :



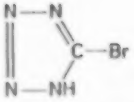
$1{,}3 \cdot 10^{-5}$	Zimmer-temp.	**E3b**	unsicher.	L19

1025 5-Chlor-Tetrazol:



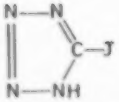
$8{,}5 \cdot 10^{-3}$	Zimmer-temp.	**E3b**	unsicher.	L19

1026 5-Brom-Tetrazol:

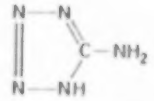
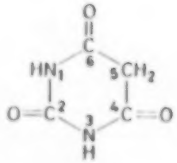


$7{,}4 \cdot 10^{-3}$	Zimmer-temp.	**E3b**	unsicher.	L19

1027 5-Jod-Tetrazol:



$1{,}4 \cdot 10^{-3}$	Zimmer-temp.	**E3b**	unsicher.	L19

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
1028	5-Amino-Tetrazol: 					
	$1 \cdot 10^{-8}$	Zimmertemp.		**E3b**	unsicher.	L19
	Barbitursäure und Derivate:					
	Allgemeine Formel: 					
1029	Barbitursäure					
	pK_1 4,035	25		**O5**	zuv.	B35
1030	1-Methyl-Barbitursäure					
	pK_1 4,348	25		**O5**	zuv.	B35
1031	1,3-Dimethyl-Barbitursäure					
	pK_1 4,679	25		**O5**	zuv.	B35

1032 5,5-Diäthyl-Barbitursäure

pK_1	8,3971	0	$\mathcal{J} = 0{,}007$ bis 0,05	**E1a**	sehr zuv.	M8a
	8,3040	5				
	8,2171	10				
	8,1367	15				
	8,0592	20				
	7,9798	25				
	7,9092	30				
	7,8471	35				
	7,7858	40				
	7,7290	45				
	7,6776	50				
	7,6264	55				
	7,5762	60				
pK_1	7,97	25		**O5**	zuv.	B35
pK_2	13,31	38	$\mathcal{J} = 0{,}1$	**O5**	unsicher. K_c-Werte.	B56
					Weitere Messungen: B51a; B57; M20a.	

1033 5-iso-Propyl-Barbitursäure

pK_1	4,94	25		**O5**	rel. zuv.	B35

1034 1,5-Dimethyl-5-Cyclohexyl-Barbitursäure

pK_1	8,37	25		**O5**	unsicher. Nähere Angaben fehlen.	B35

1035 5-Methyl-5-Phenyl-Barbitursäure

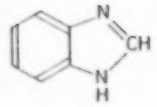
pK_1	7,73	25		**O5**	unsicher. Nähere Angaben fehlen.	B35

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
1036	5-Äthyl-5-Phenyl-Barbitursäure					
	pK_1 7,45	25		**O5**	unsicher. Nähere Angaben fehlen.	B35
1037	5-Äthyl-5-iso-Pentyl-Barbitursäure					
	pK_1 7,96	25		**O5**	unsicher. Nähere Angaben fehlen.	B35
1038	5-Allyl-5-iso-Propyl-Barbitursäure					
	pK_1 7,99	25		**O5**	unsicher. Nähere Angaben fehlen.	B35
1039	5-Allyl-5-n-Butyl-Barbitursäure					
	pK_1 7,98	25		**O5**	unsicher. Nähere Angaben fehlen.	B35
					Weitere Messungen an Barbitursäurederivaten: B56.	
1040	5-Allyl-5-iso-Butyl-Barbitursäure					
	pK_1 7,79	25		**O5**	unsicher. Nähere Angaben fehlen.	B35

1041 5,5-Diallyl-Barbitursäure

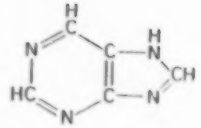
pK_1 7,77	25	**O5**	unsicher. Nähere Angaben fehlen.	B35

1042 Benziminazol:



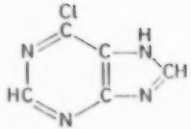
pK_1 5,30 pK_2 12,3	25	**E3b** **D1**	unsicher.	T1

1043 Purin:

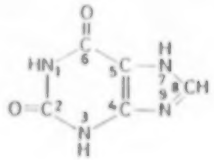


pK_1 2,52 pK_2 8,92	25	**O5**	unsicher.	B22

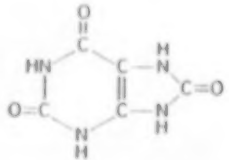
1044 6-Chlor-Purin:



pK 7,68	25	**O5**	unsicher.	B22

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
1045	Xanthin: 					
	pK_1 7,53 pK_2 11,63		$\mathcal{I} = 0{,}05$	**O5**	unsicher.	C8
	pK_1 7,7			**E3b**	unsicher.	O2
					Weitere Messung: R7.	
1046	1-Methyl-Xanthin					
	pK_1 7,70 pK_2 12,0	25		**E3b** **D1**	unsicher.	T1
	pK_1 7,7			**E3b**	unsicher.	O2
1047	3-Methyl-Xanthin					
	pK_1 8,10 pK_2 11,3	25		**E3b** **D1**	unsicher.	T1
	pK_1 8,5			**E3b**	unsicher.	O2
	pK_1 8,32 pK_2 11,9		$\mathcal{I} = 0{,}05$	**O5**	unsicher.	C8
					Weitere Messungen: R7.	

1048	7-Methyl-Xanthin				
	pK_1 8,33 $pK_2 \simeq 13$	$J = 0{,}05$	**O5**	unsicher.	C3
	pK_1 8,30	25	**E3b** **D1**	unsicher.	T1
	pK_1 8,5		**E3b**	unsicher.	O2
				Weitere Messungen: R7.	
1049	9-Methyl-Xanthin				
	pK_1 6,25	25	**E3b** **D1**	unsicher.	T1
	pK_1 6,3		**E3b**	unsicher.	O2
1050	1,3-Dimethyl-Xanthin				
	pK_1 8,81	$J = 0{,}05$	**O5**	unsicher.	C3
	pK_1 8,6		**E3b**	unsicher.	O2
				Weitere Messungen: R7.	
1051	1,7-Dimethyl-Xanthin				
	pK_1 8,71	$J = 0{,}05$	**O5**	unsicher.	C3
	pK_1 8,5		**E3b**	unsicher.	O2
				Weitere Messungen: R7.	
1052	1,9-Dimethyl-Xanthin				
	pK_1 6,3		**E3b**	unsicher.	O2
1053	3,7-Dimethyl-Xanthin				
	pK_1 9,9		**E3b**	unsicher.	O2
	pK_1 9,97	$J = 0{,}05$	**O5**	unsicher.	C3

No.	*Name, Formel u. Dissoziationskonstante K*	*T* (°C)	*Bemerkungen*	*Methode*	*Kritik*	*Lit.*
1054	Adenin (6-Amino-Purin)					
	pK_1 4,15 pK_2 9,80	25		**E3b** **D1**	unsicher.	T1
1055	Guanin (2-Amino-6-Oxy-Purin)					
	pK_1 3,3 pK_2 9,2 pK_3 12,3	25		**E3b** **D1**	unsicher.	T1
1056	Harnsäure: 					
	K_1 4,01·10⁻⁶ K_2 2,88·10⁻⁸			**E3b** **D1**	unsicher. K_c-Werte.	B25a

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I. TABLES FOR THE CALIBRATION OF GRATING SPECTROMETERS IN THE RANGE 4300–600 cm^{-1}

INTRODUCTION

In the past five years, the number of grating infra-red spectrometers has greatly increased. Most of the recent instruments operate mainly in the range 4000–600 cm^{-1} and have a limit of resolution between 0·1 and 1 cm^{-1}. Often, these spectrometers are not equipped for precise wavelength determination by measurement of the grating angle, and for them it is necessary, and for the others which *are* so equipped it is desirable, to have standard wavenumbers for calibration.

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The precision with which a wavelength or wavenumber can be measured improves with better resolution. For a given instrument this precision can be seriously affected by mechanical instability, temperature variation and other non-spectroscopic factors. However, if it is limited only by the experimenter's ability to locate the maximum of a sharp absorption line the shape of which is determined by the slit function of an energy-limited spectrometer, the precision is likely to be from one-fifth to one-tenth of the achievable resolution. That is, a spectrometer whose best resolution is about 0·3 cm^{-1} will be capable of a wavenumber precision of about $\pm$ 0·03–0·06 cm^{-1}. Thus the wavenumber standards to be used for the calibration of such spectrometers should have an absolute accuracy of $\pm$ 0·03 cm^{-1} or better.

Until quite recently no measurements in the infra-red from 2000 to 600 cm^{-1}, and very few from 4000 to 2000 cm^{-1}, were of this accuracy. It was therefore necessary to use higher orders of atomic emission lines for calibration, a procedure capable of high accuracy but having many pitfalls and inconveniences. With the extension of precise measurement to lower wavenumbers by several laboratories in various countries, it has become possible to compare the wavenumber values for molecular absorption bands determined with respect to different standards of higher-order emission and absorption lines in different laboratories, and thereby to assess the absolute accuracy of these measurements.

In view of the urgent need for wavenumber standards in the infra-red, the Commission on Molecular Spectroscopy has made such an assessment of existing data (including certain measurements carried out specifically for the Commission), and is presenting the results without delay in the following tables of *provisional wavenumbers*. The Commission does not regard the data in these tables as *standard*, since they have not met tests usually required of standard wavelengths in the visible region. Moreover, the accuracy of the molecular data will undoubtedly be improved in the next few years. However, until more powerful spectrometers for the region below 2000 cm^{-1} are

built and a broader effort can be made in the measurement, evaluation and tabulation of standard wavenumbers, these tables are believed to represent very nearly the best that can be done with existing data. They are considered to be reliable to $\pm 0{\cdot}03$ cm^{-1} or better, except in those cases where for one reason or another as stated, the values are less accurate.

SOURCES OF DATA FOR THE TABLES

The molecular data in these tables are presented as wavenumbers in cm^{-1} *in vacuo*. The Commission believes that there are important reasons for the use of wavenumbers rather than wavelengths in infra-red spectroscopy. The wavenumber values, being values calculated from wavelengths measured in air, are of course dependent in accuracy on the accuracy with which the refractive index of air is known. Since the latter accuracy is considerably better than that of standard infra-red wavelengths, the accuracy of the calculated wavenumbers is not inferior to that of the observed wavelengths.

Standard infra-red wavelengths of atomic emission spectra are essential in the determination of wavenumber values of molecular absorption lines. These wavelengths may also prove useful for calibration of grating spectrometers in the range 10,000–4,000 cm^{-1}. For this reason tables of standard wavelengths in air in the range 1–2·5 μ and their calculated wavenumbers in cm^{-1} *in vacuo* are included herewith. A complete table for conversion of wavelengths in air to wavenumbers is also given for the range 1–20 μ (10,000–500 cm^{-1}).

STANDARD WAVELENGTHS AND WAVENUMBERS OF ATOMIC EMISSION LINES

In 1907 the International Union for Co-operation in Solar Research adopted[1] as the primary standard of wavelength the red cadmium line with the wavelength specified as 6438·4696 Å for standard air. Recently, the orange line of krypton-86 has been measured near the triple point of nitrogen in several laboratories, and the wavelength has been reported[2] to be 6057·8021 Å for vacuum, 6056·1252 Å for standard air, relative to the red line of cadmium. The krypton-86 line was adopted as the primary standard for all length measurements by the General Conference on Weights and Measures, meeting at Paris in October, 1960.

In 1950 Meggers and Westfall[3] devised a simple tube containing mercury-198 which emits sharp lines when the vapour is excited by an electrode-less, high-frequency discharge. Meggers and others have measured the wavelength of the green mercury line with very high precision and the accepted wavelength is 5460·7532 Å for standard air[4]. There are several features which make the mercury-198 lamp well suited for laboratory use. The lamp is rugged, of long life and easy to operate, and the green line is intense and readily isolated. For these reasons the green line of mercury-198 is recommended as a laboratory standard for all spectroscopic wavelength measurements. A very small pressure shift which has been observed in the position of this line is produced by the action of the carrier gas, but in ordinary uses this effect need not be taken into consideration. The mercury-198 lamp with the high-frequency discharge equipment can be obtained from commercial sources.

Many atomic lines have been measured with high precision by the use of a Fabry-Perot interferometer, and these lines, which fall mainly in the visible and ultra-violet regions, can be used in higher orders for calibrating infra-red spectrometers. The iron spectrum has been used as a secondary standard for many years, and by 1955 precise measurements were reported[5] from several laboratories on 575 iron lines between 2500 and 9400 Å. In 1957 Stanley and Meggers[6] reported the wavelengths of 103 iron lines measured with a Fabry-Perot interferometer in the range from 2900 to 4100 Å. In view of the wide availability of tables of wavelengths of the iron lines, they will not be included here.

The spectra of the rare gases are rich in lines in the visible and near infra-red regions. A large number of lines in these gases have been measured with a Fabry-Perot interferometer by Meggers and Humphreys[7]. Paul and Humphreys[8] have extended the interferometric measurements of the spectrum of neon, argon, and krypton to 2 μ. Recently Burns, Adams and Longwell[9] have made many determinations of the wavelengths of the lines of neon. The wavelengths listed in *Table A* are mainly from their work, except for some lines which are from the references 7–11. *Table B* gives additional neon wavelengths which have been calculated by the combination principle[11]. Also, Burns and Adams[10] have made many measurements of the wavelengths of the lines of argon. Their values are listed in *Table C* with some additional lines by other workers.

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Tables C, D and E list the intense lines of argon, krypton and xenon with wavelengths greater than 7000 Å. The listed values are experimentally determined except in a few cases where calculated values are added. By the use of the combination principle the wavelengths of a number of lines entered in the tables have been calculated. The agreement with the experimental values is excellent. The calculated values are given in references 5, 10 and 11. Additional lines with wavelengths less than 5800 Å can be found in the paper of Meggers and Humphreys[7]. Rao, Coburn, Garing, Rossman and Nielsen[12] have used the higher orders of the visible lines of neon for calibration in the region from 10 to 20 μ. As is well known, the intercomparison of higher orders in some gratings has led in the past to errors on account of imperfections of the optical properties of the grating. However, with modern gratings of high quality, the use of higher orders is quantitatively satisfactory.

Several lines of mercury-198 have been measured with a Fabry-Perot interferometer in the infra-red region by Paul and Humphreys[8], Rank and co-workers[13], and Peck[14]. The results reported in these papers are listed in *Table F*.

There are a number of lines in the infra-red region which have been measured by a comparison spectrum but not with an interferometer. It is estimated that they are, on the average, correct to one part in 100,000 ($\sim$0·1 cm^{-1}). These lines have been reported by Plyler, Blaine, and Tidwell[15], Meggers[16], and Humphreys and Kostkowski[17]. A selected list of these lines is given in *Table G*. It should be emphasized that these lines should not be used for high precision measurement, especially in the regions where more precisely measured lines of neon, argon, krypton, xenon and mercury-198 are available. They are useful in higher orders since the uncertainty of the wavenumber is inversely proportional to the grating order.

Discharge tubes containing various gases can be obtained from several commercial suppliers. Hollow-cathode tubes containing one or more rare gases have also been designed and used for sources[12,19]. The hollow-cathode source has been used for the iron spectrum in place of the open-air arc. Stanley and Meggers[6] have shown that a tube containing $FeBr_3$ and helium at 2 mm pressure emits very sharp iron lines when excited by a high frequency generator. Relatively intense spectra of the rare gases can be obtained by the use of a low pressure electrode-less tube excited by a microwave source.

Table A. Intense emission lines of neon, 5800–9700 Å, experimentally measured

λ_{air} (Å)	ν (cm^{-1})	λ_{air} (Å)	ν (cm^{-1})
5852·4878	17082·016	8128·9077	12298·394
5881·8950	16996·613	8136·4061	12287·060
5913·633	16905·394	8248·6812	12119·819
5944·8342	16816·669	8259·3795	12104·120
5965·474	16758·486	8266·0788	12094·310
5974·628	16732·809	8267·1166	12092·792
5975·5340	16730·272	8300·3248	12044·411
5987·9069	16695·701	8365·7464	11950·222
6029·9971	16579·165	8377·6062	11933·305
6074·3377	16458·144	8417·1614	11877·227
6096·1630	16399·221	8418·4265	11875·441
6128·4498	16312·826	8463·3569	11812·397
6143·0623	16274·023	8484·4424	11783·042
6163·5939	16219·8123	8495·3591	11767·900
6182·146	16171·138	8544·6952	11699·954
6217·2813	16080·752	8571·3535	11663·595
6266·4950	15953·471	8591·2583	11636·542
6304·7893	15856·573	8634·6472	11578·068
6334·4279	15782·381	8647·0400	11561·475
6382·9914	15662·306	8654·3837	11551·664
6402·2460	15615·202	8655·5206	11550·148
6506·5279	15364·935	8679·4898	11518·250
6532·8834	15302·949	8681·9216	11515·024
6598·9529	15149·735	8704·1132	11485·671
6652·0925	15028·714	8771·6592	11397·222
6678·2764	14969·790	8780·6223	11385·588
6717·430	14883·394	8783·7539	11381·528
6929·4672	14427·144	8830·9078	11320·756
7024·0500	14232·876	8853·8669	11291·399
7032·4128	14215·950	8865·3057	11276·831
7059·1079	14162·191	8865·7562	11276·257
7173·9380	13935·505	8919·4987	11208·314
7245·1665	13798·503	9486·680	10538·205
7438·8981	13439·150	9534·164	10485·721
7488·8712	13349·472	9665·424	10343·321
7535·7739	13266·384		
7544·0439	13251·841		
7943·1805	12585·954		
8082·4576	12369·074		
8118·5495	12314·085		

Table B. Additional intense neon lines calculated from energy levels derived from interferometric measurements

λ_{air} (Å)	ν (cm^{-1})	λ_{air} (Å)	ν (cm^{-1})
8301·557	12042·623	19573·664	5107·511
8376·359	11935·081	19577·045	5106·629
8778·732	11388·039	20350·153	4912·625
9148·670	10927·552	21708·060	4605·327
9201·757	10864·509	22247·379	4493·685
9220·057	10842·948	22428·125	4457·471
9221·578	10841·156	22466·845	4449·789
9226·690	10835·150	22530·281	4437·261
9275·517	10778·113	22661·688	4411·530
9300·852	10748·754	23260·164	4398·023
9310·584	10737·519	23565·267	4242·376
9313·971	10733·614	23636·375	4229·613
9326·504	10719·190	23701·698	4217·956
9373·308	10665·666	23707·651	4216·897
9425·379	10606·743	23709·061	4216·646
9433·005	10598·168	23978·161	4169·324
9459·209	10568·809	24098·598	4148·487
9547·406	10471·177	24161·476	4137·691
10562·408	9464·945	24218·996	4127·864
11143·018	8971·773	24364·937	4103·139
11177·531	8944·070	24371·637	4102·011
11390·440	8776·889	24447·900	4089·215
11525·016	8674·403	24459·451	4087·284
11536·346	8665·883	24459·714	4087·240
11688·008	8553·437	24776·510	4034·980
11789·041	8480·133	24903·795	4014·357
11789·895	8479·519	24928·932	4010·309
12066·341	8285·249	25161·733	3973·205
12459·386	8023·883	25524·212	3916·780
12595·001	7937·486		
12689·199	7878·563		
12769·534	7828·998		
12912·023	7742·602		
13219·251	7562·657		
17161·938	5825·257		

Table C. Intense emission lines of argon, 6900–17,000 Å

λ_{air} (Å)	ν (cm^{-1})	λ_{air} (Å)	ν (cm^{-1})
6965·4304	14352·656	11488·108*	8702·271
7030·262	14220·300	11668·708	8567·584
7067·2175	14145·940	12112·323	8253·796
7147·0408	13987·950	12139·735	8235·158
7272·9349	13745·821	12343·390	8099·286
7372·117	13560·889	12402·826	8060·473
7383·9800	13539·103	12439·318	8036·827
7503·8676	13322·793	12456·112	8025·991
7514·6514	13303·674	12487·661	8005·715
7635·1053	13093·792	12702·278	7870·450
7723·7599	12943·500	12733·414	7851·206
7724·2064	12942·752	12802·737	7808·694
7891·075	12669·060	12933·190	7729·930
7948·1755	12578·045	12956·656	7715·930
8006·1566	12486·953	13008·260	7685·321
8014·7853	12473·511	13213·989	7565·668
8053·307	12413·845	13228·103	7557·596
8103·6920	12336·663	13230·891	7556·003
8115·3109	12319·000	13272·632	7532·241
8264·5209	12096·590	13313·206	7509·285
8408·2094	11889·872	13367·109	7479·004
8424·6473	11866·673	13406·586	7456·981
8521·4407	11731·881	13504·188	7403·086
8667·9430	11533·594	13599·333	7351·292
9122·9660	10958·340	13622·654	7338·707
9224·498	10837·724	13678·546	7308·720
9354·218	10687·432	13718·575	7287·394
9657·7841	10351·504	14093·635	7093·462
9784·5010	10217·443	15046·503	6644·247
10470·053*	9548·433	15301·879	6533·360
10478·033	9541·162	16180·017*	6178·775
10673·566	9366·374	16940·578	5901·374
10681·771	9359·180	17914·627*	5580·507
11078·867	9023·723	17914·723*	5580·477
11441·830	8737·469	25505·237*	3919·694
		25661·035*	3895·895

* Calculated values.

Table D. Intense emission lines of krypton, 7400–20,000 Å

λ_{air} (Å)	ν (cm^{-1})
7486·862	13353·053
7587·4130	13176·096
7601·5443	13151·602
7685·2460	13008·365
7694·5395	12992·654
7854·8217	12727·532
8059·5038	12404·301
8104·3642	12335·640
8112·902	12322·658
8190·0543	12206·576
8263·2398	12098·465
8281·0495	12072·446
8298·1077	12047·629
8508·8700	11749·214
8776·7490	11390·612
8928·6920	11196·774
9751·759	10251·749
11819·374	8458·370
13177·403	7586·674
13622·404	7338·841
13634·215	7332·484
14426·786	6929·657
14734·440	6784·966
15239·608	6560·056
15334·966	6519·264
16785·127	5956·028
16853·490	5931·869
16890·444	5918·891
16896·744	5916·684
16935·799	5903·040
18002·222	5553·353
18167·320	5502·887

Table E. Intense emission lines of xenon, 7000–10,000 Å

λ_{air} (Å)	ν (cm^{-1})
7119·598	14041·866
7285·301	13722·488
7316·272	13664·398
7321·452	13654·731
7386·003	13535·395
7393·793	13521·134
7584·680	13180·843
7642·025	13081·936
7802·651	12812·631
7881·320	12684·741
7887·3898	12674·979
7967·342	12547·786
8057·258	12407·758
8061·339	12401·477
8206·336	12182·358
8231·6336	12144·919
8280·1162	12073·807
8346·8217	11977·317
8409·1894	11888·486
8739·372	11439·328
8819·411	11335·512
8952·2506	11167·309
9045·4460	11052·253
9162·6520	10910·876
9513·377	10508·631
9799·697	10201·600
9923·198	10074·635

Table F. Intense emission lines of ^{198}Hg, 10,000–18,000 Å

λ_{air} (Å)	ν (cm^{-1})
10139·793	9859·432
11287·406	8857·006
12071·604	8281·568
13570·573	7366·870
13673·398	7311·471
15295·976	6535·882
16920·659	5908·322
16942·474	5900·714
17073·120	5855·561
17109·893	5842·976

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Table G. Additional emission lines of argon, neon, krypton, xenon, and Hg, 7600–40,000 Å, accurate to ±0·10 cm^{-1} but not measured with an interferometer

Gas	λ_{air} (Å)	ν (cm^{-1})	*Gas*	λ_{air} (Å)	ν (cm^{-1})
Xe	7643·91	13078·71	Ne	18591·12	5377·44
Xe	8648·54	11559·47	Ne	18597·30	5375·66
Xe	8862·32	11280·63	Xe	18788·13	5321·06
Xe	8908·73	11221·87	A	19817·54	5044·66
Xe	8987·57	11123·43	Kr	20209·87	4946·73
Xe	9374·76	10664·01	Xe	20262·28	4933·93
Kr	10593·01	9437·60	Kr	20423·93	4894·88
Ne	10620·70	9413·00	A	20616·21	4849·23
Xe	10706·78	9337·32	A	20986·10	4763·76
Xe	10758·86	9292·12	Kr	21165·14	4723·46
Ne	10798·06	9258·39	Xe	21470·00*	4656·39
Xe	10838·34	9223·98	A	21534·16	4642·52
Ne	10844·49	9218·75	Kr	21902·51	4564·44
Kr	10874·92	9192·95	A	22077·20	4528·32
Xe	10895·32	9175·74	Kr	22485·52	4446·09
Xe	11085·25	9018·53	Hg	22493·28	4444·56
Xe	11127·20	8984·53	Xe	23193·28*	4310·42
Kr	11257·74	8880·35	Hg	23253·07	4299·33
Ne	11409·24	8762·43	Kr	23340·07	4283·31
Kr	11457·52	8725·50	Ne	23372·81	4277·31
Ne	11522·82	8676·06	Kr	23502·55	4253·70
Xe	12623·36	7919·65	A	23845·13	4192·58
Xe	13657·22	7320·13	Kr	24260·54	4120·80
Kr	13738·94	7276·59	Kr	24292·16	4115·43
Kr	13883·15	7201·01	Xe	24824·63*	4027·14
Kr	13924·11	7179·82	A	25125·08	3979·00
Xe	14241·23	7019·95	Kr	25233·77	3961·86
Kr	14347·69	6967·86	Xe	26268·95*	3805·74
Xe	14732·88	6785·68	Xe	26510·96*	3771·00
Xe	15418·12	6484·10	Hg	32148·06	3109·76
Xe	17325·79	5770·17	Hg	36303·03	2753·84
Kr	17367·80	5756·21	Hg	39283·61	2544·90
Ne	18082·71	5528·63			
Ne	18276·59	5469·99			
Ne	18282·58	5468·20			
Ne	18304·00	5461·79			
Ne	18385·17	5437·68			
Ne	18390·10	5436·22			
Ne	18403·16	5432·37			
Ne	18422·43	5426·68			

* Calculated values.

In the measurement of the higher orders of atomic lines in the infra-red region, the intensities observed will vary with the source and the method of excitation. However, the greatest variation of intensity arises from the characteristics of the grating used. The first-order spectrum may be weak and the higher orders intense, or some high orders may be very weak. The intensity of a line may be misleading and the position or wavelength should be the key to identification. An example of the changes in intensity with the order in which the gratings are used is shown in *Figures A* and *B*. In *Figure A*

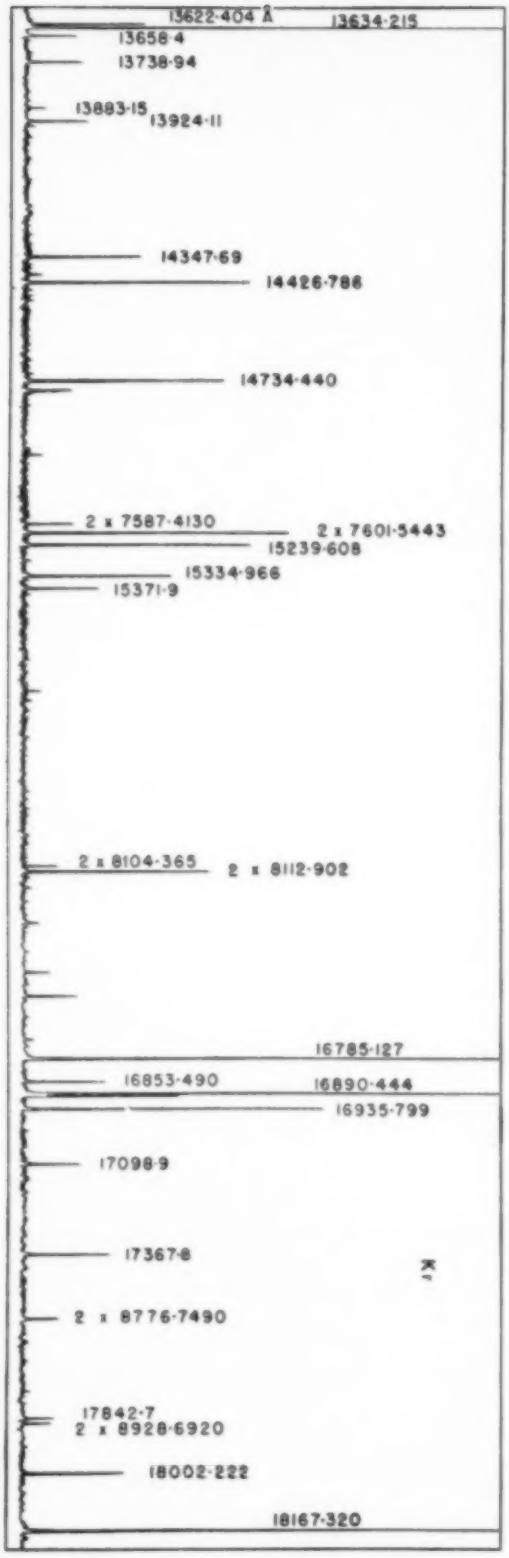

Figure A. The first- and second-order lines of krypton in the region from 1·36 to 1·82 μ as observed with a grating of 15,000 lines/in.

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Figure B. The second- and fourth-order lines of krypton in the region from 3·2 to 3·7 μ as observed with a 7500 lines/in. grating

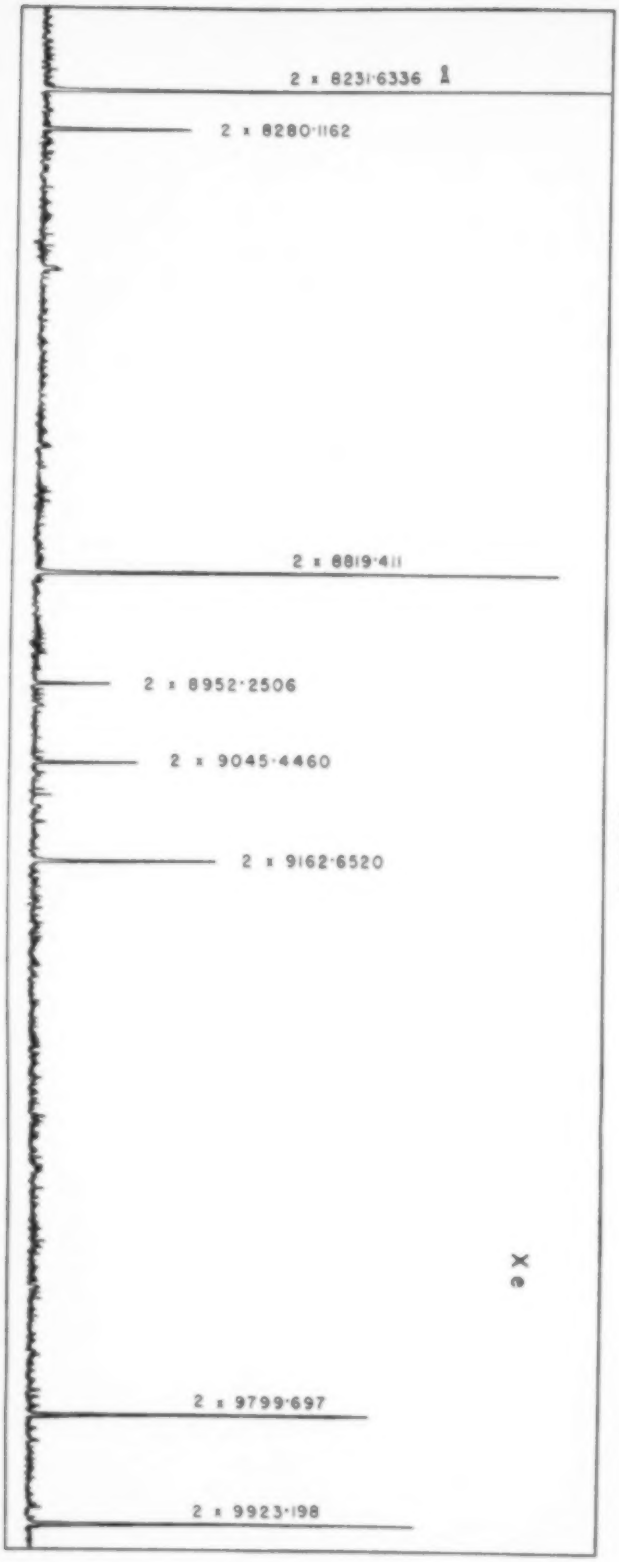

Figure C. The second-order lines of xenon in the region from 1·6 to 2 μ as observed with a 10,000 lines/in. grating

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some first- and second-order lines of krypton are recorded in the region from 1·36 to 1·82 μ with a grating ruled with 15,000 lines/in. In *Figure B* some of the same lines are recorded in the second- and fourth-orders of a grating having 7500 lines/in. A comparison of these two figures shows that the higher order lines are less intense with the grating of 15,000 lines/in. than with the one having 7500 lines/in., the influence of the grating being especially noticeable in the observed intensities of the higher orders of lines from 7500 to 9000 Å. A part of the xenon spectrum is shown in *Figure C*. There are no intense first-order lines in the region from 1·6 to 2 μ but a number of second-order lines are observed.

REFRACTIVE INDICES OF AIR

Wavelengths of lines have usually been measured in air and in order to compare work carried out in different laboratories final results are reduced to standard air. Standard air is defined as dry air at a pressure of 760 mm Hg and at a temperature of 15°C, having 0·03 per cent CO_2 by volume. These conditions are not usually fulfilled in the laboratory, and a reduction of the data taken under conditions differing from those of standard air must be made. Penndorf[20] has given an equation for the influence of pressure and temperature on the index of refraction of air, which is:

$$(n - 1) = (n_s - 1)\frac{1 + \alpha t_s}{1 + \alpha t}\frac{P}{P_s}$$

where $t_s = 15°C$, t = temperature in °C of the air surrounding the dispersing element, P = atmospheric pressure in laboratory in mm, $P_s = 760$ mm, n_s is the index of refraction of standard air and n is the index of refraction at $t°$ and P mm. The optical temperature coefficient, denoted by α, has the approximate value 0·00366. Small changes in CO_2 content and the humidity of the air do not appear to change the indices of air appreciably. No extensive tables have been provided for these corrections and they are usually neglected. However, in the future when experimental values of the indices of refraction are determined in the neighbourhood of 2·7, 4·3 and 6·2 μ, a detectable effect may be observed for changes in the amount of water vapour and CO_2 in the air.

The influence of temperature on the refractive index of air is appreciable, and temperature corrections must be made. Penndorf[20] has calculated a table which gives the value of the indices of refraction of air from 0·2 to 20·0 μ for temperatures ranging from −30°C to +30°C. For example, at 15°C, $(n - 1) \times 10^8$ is 27,277 and at 30°C, is 25,925, for 3 μ radiation. If the air temperature were 30°C and the refractive index of air at 15°C were used for reducing the data to cm^{-1}, an error of 0·045 cm^{-1} would result.

For many years Kayser's "Tabellen der Schwingungszahlen" have served as a ready means for reducing wavelengths in air to cm^{-1} in vacuum. These tables did not extend past 1·0 μ, but Babcock[21] demonstrated how they could be used further in the infra-red region, and gave a table of corrections.

In recent years new measurements on the refractive index of air have shown that the formula used by Kayser for the calculation of his table was not

Table H. Wavelength-to-wavenumber conversion tables and refractive index of standard air, 2–20 μ

Wavelength (μ)	ν_{vac} (cm^{-1})	*Index* $(n-1) \times 10^8$ *for* 15°C	*Wavelength* (μ)	ν_{vac} (cm^{-1})	*Index* $(n-1) \times 10^8$ *for* 15°C
2·00000	4998·636	272984	2·90000	3447·336	272782
·02	4949·144	976	·92	23·724	779
·04	4900·623	969	·94	00·433	777
·06	4853·044	961	·96	3377·457	774
·08	4806·380	955	·98	54·790	772
2·10000	4760·605	272948	3·00000	3332·424	272770
·12	4715·694	941	·02	10·355	767
·14	4671·622	935	·04	3288·577	765
·16	4628·367	929	·06	67·083	763
·18	4585·904	923	·08	45·868	761
2·20000	4544·214	272917	3·10000	3224·927	272759
·22	4503·276	911	·12	04·254	757
·24	4463·068	905	·14	3183·845	755
·26	4423·572	900	·16	63·694	753
·28	4384·768	895	·18	43·797	751
2·30000	4346·640	272890	3·20000	3124·148	272749
·32	4309·169	885	·22	04·743	747
·34	4272·339	880	·24	3085·578	745
·36	36·132	875	·26	66·648	744
·38	00·535	870	·28	47·949	742
2·40000	4165·530	272866	3·30000	3029·477	272740
·42	4131·104	862	·32	11·227	738
·44	4097·243	857	·34	2993·196	737
·46	63·932	853	·36	75·379	735
·48	31·158	849	·38	57·773	734
2·50000	3998·909	272845	3·40000	2940·375	272732
·52	67·172	841	·42	23·179	730
·54	35·934	837	·44	06·184	729
·56	05·185	834	·46	2889·385	727
·58	3874·912	830	·48	72·780	726
2·60000	3845·105	272826	3·50000	2856·364	272724
·62	15·753	823	·52	40·135	723
·64	3786·846	820	·54	24·089	722
·66	58·373	816	·56	08·223	720
·68	30·326	813	·58	2792·535	719
2·70000	3702·694	272810	3·60000	2777·021	272718
·72	3675·468	807	·62	61·678	716
·74	48·640	804	·64	46·504	715
·76	22·200	801	·66	31·496	714
·78	3596·141	798	·68	16·651	712
2·80000	3570·455	272795	3·70000	2701·966	272711
·82	45·132	792	·72	2687·439	710
·84	20·167	790	·74	73·068	709
·86	3495·550	787	·76	58·849	708
·88	71·275	784	·78	44·781	707

Table H. (continued)

Wavelength (μ)	$\nu_{vac.}$ (cm^{-1})	*Index* $(n-1) \times 10^6$ *for* 15°C	*Wavelength* (μ)	$\nu_{vac.}$ (cm^{-1})	*Index* $(n-1) \times 10^6$ *for* 15°C
3·80000	2630·862	272705	5·00000	1999·455	272660
·82	17·087	704	·05	79·658	659
·84	03·457	703	·10	60·250	658
·86	2589·967	702	·15	41·218	657
·88	76·617	701	·20	22·553	656
3·90000	2563·404	272700	5·25000	1904·243	272655
·92	50·325	699	·30	1886·278	654
·94	37·379	698	·35	68·649	653
·96	24·564	697	·40	51·347	652
·98	11·878	696	·45	34·362	651
4·00000	2499·319	272695	5·50000	1817·686	272650
·025	83·795	694	·55	01·311	649
·050	68·463	693	·60	1785·228	648
·075	53·319	692	·65	69·429	647
·100	38·360	690	·70	53·908	646
·125	23·582	689			
·150	08·982	688	5·75000	1738·656	272645
·175	2394·557	687	·80	23·668	645
			·85	08·936	644
4·20000	2380·303	272686	·90	1694·453	643
·225	66·219	685	·95	80·214	642
·250	52·300	684			
·275	38·544	683	6·00000	1666·212	272642
·300	24·947	682	·05	52·442	641
·325	11·508	681	·10	38·897	640
·350	2298·224	680	·15	25·573	640
·375	85·091	679	·20	12·464	639
4·40000	2272·108	272678			
·425	59·271	677	6·25000	1599·564	272638
·450	46·578	677	·30	86·869	638
·475	34·028	676	·35	74·374	637
·500	21·616	675	·40	62·074	637
·525	09·342	674	·45	49·965	636
·550	2197·203	673			
·575	85·197	672	6·50000	1538·042	272635
			·55	26·301	635
4·60000	2173·321	272672	·60	14·739	634
·625	61·573	671	·65	03·350	634
·650	49·951	670	·70	1492·131	633
·675	38·454	669			
·700	27·080	669	6·75000	1481·078	272633
·725	15·825	668	·80	70·187	632
·750	04·689	667	·85	59·456	632
·775	2093·670	666	·90	48·880	631
			·95	38·457	631
4·80000	2082·765	272666			
·825	71·974	665	7·00000	1428·182	272630
·850	61·294	664	·05	18·053	630
·875	50·723	664	·10	08·067	629
·900	40·260	663	·15	1398·220	629
·925	29·903	662	·20	88·510	629
·950	19·651	662			
·975	09·502	661			

Table H. (continued)

Wavelength (μ)	ν_{vac} (cm^{-1})	*Index* $(n-1)\times 10^6$ *for* 15°C	*Wavelength* (μ)	ν_{vac} (cm^{-1})	*Index* $(n-1)\times 10^6$ *for* 15°C
7·25000	1378·934	272628	11·5000	869·328	272611
·30	69·490	628	·6	61·834	610
·35	60·173	627	·7	54·468	610
·40	50·983	627	·8	47·227	610
·45	41·916	627	·9	40·107	610
7·50000	1332·970	272626	12·0000	833·106	272610
·55	24·142	626	·1	26·221	610
·60	15·431	626	·2	19·449	609
·65	06·833	625	·3	12·787	609
·70	1298·347	625	·4	06·232	609
7·75000	1289·971	272625	12·5000	799·782	272609
·80	81·702	624	·6	93·435	609
·85	73·538	624	·7	87·187	609
·90	65·478	624	·8	81·037	608
·95	57·519	623	·9	74·983	608
8·00000	1249·659	272623	13·0000	769·021	272608
·1	34·231	622	·2	57·369	608
·2	19·180	622	·4	46·065	608
·3	04·491	621	·6	35·094	607
·4	1190·152	621	·8	24·440	607
8·50000	1176·150	272620	14·0000	714·091	272607
·6	62·474	620	·2	04·033	607
·7	49·112	619	·4	694·255	606
·8	36·054	619	·6	84·745	606
·9	23·289	618	·8	75·492	606
9·00000	1110·808	272618	15·0000	666·485	272606
·1	1098·602	618	·2	57·715	606
·2	86·660	617	·4	49·174	606
·3	74·976	617	·6	40·851	605
·4	63·540	616	·8	32·739	605
9·50000	1052·345	272616	16·0000	624·830	272605
·6	41·383	616	·2	17·116	605
·7	30·647	615	·4	09·590	605
·8	20·130	615	·6	02·245	605
·9	09·826	615	·8	595·076	604
10·0000	999·727	272614	17·0000	588·075	272604
·1	89·829	614	·2	81·237	604
·2	80·125	614	·4	74·556	604
·3	70·609	614	·6	68·027	604
·4	61·276	613	·8	61·645	604
10·5000	52·121	272614	18·0000	555·404	272604
·6	43·139	613	·2	49·301	604
·7	34·325	612	·4	43·330	604
·8	25·674	612	·6	37·488	603
·9	17·181	612	·8	31·770	603
11·0000	908·843	272612	19·0000	526·172	272603
·1	900·655	611	·2	20·691	603
·2	892·614	611	·4	15·323	603
·3	84·715	611	·6	10·065	603
·4	76·954	611	·8	04·913	603
			20·0000	499·864	272603

accurate. In 1953, Edlén[22] proposed the following relation for the indices of refraction of standard air:

$$(n_s - 1)\ 10^8 = 6432{\cdot}8 + \frac{2{,}949{,}810}{146 - \nu^2} + \frac{25{,}540}{41 - \nu^2}$$

ν is the vacuum wavenumber in μ^{-1}, that is, $\nu = 1/(\lambda$ in microns).

From Edlén's formula, Coleman, Bozman and Meggers[23] have calculated conversion tables for wavelengths in air to wavenumbers in vacuum for the region from 2000 Å to 1000 μ. These tables should be of great value in the reduction of wavelengths measured in air to cm^{-1} in vacuum. In *Table H* are given a few values quoted from Vol. 2 of the above mentioned tables for the region from 2–20 μ.

When unknown wavelengths are measured in a grating spectrometer in air with respect to standard wavelengths in a different grating order, it is of course necessary to use the index of refraction of air at the corresponding wavelengths to obtain the wavenumbers. The procedure for doing this is described on p. 555 in the section "Procedures for the Use of the Tables".

TABLES OF WAVENUMBERS OF INFRA-RED ABSORPTION LINES IN THE SPECTRA OF GASEOUS MOLECULES

It is important to distinguish between the precision of the data, which is a measure of their self-consistency, and the absolute accuracy, which measures both the self-consistency and the systematic error. For twenty years or more, infra-red data in the range 5000–500 cm^{-1} have been reported to $\pm 0{\cdot}01$ cm^{-1}, with a precision of $\pm 0{\cdot}1$ cm^{-1} or even better. It is only in the past eight or ten years that infra-red data have had a demonstrable absolute accuracy better than $\pm 0{\cdot}1$ cm^{-1}.

The first molecular measurements of accuracy approaching $\pm 0{\cdot}01$ cm^{-1} below 5000 cm^{-1} were those of Rank and co-workers[24] and Plyler, Allen and Tidwell[25]. These two groups independently measured the lines of the carbon monoxide overtone band at 4300–4100 cm^{-1} to 0·001 cm^{-1} and agreed on most of the measured lines to better than 0·01 cm^{-1}. The measurements were made in both laboratories with reference to standard atomic emission lines in higher grating orders. Since the absolute wavelengths of these emission lines are known to one part in five million or better, direct comparison of molecular absorption lines with them in overlapping orders is potentially capable of the same kind of accuracy (the procedures for comparison are discussed in the preceding sections and references there cited). The agreement ($\pm 0{\cdot}01$ cm^{-1}) between the results of the two sets of measurements on carbon monoxide, which are of comparable precision, is taken as a measure of their absolute accuracy.

The same methods had been applied by Plyler, Blaine and Connor[26] to the lines of the fundamental band of carbon monoxide at 2000–2250 cm^{-1}. These measurements have a precision of better than $\pm 0{\cdot}01$ cm^{-1}, and their absolute accuracy has been checked by Rank and co-workers[24] with the help of calculations based on the overtone band. The check indicates that the accuracy of the measurements on the fundamental is $\pm 0{\cdot}01$ cm^{-1}. A similar check has been made by Rank, Skorinko, Eastman and Wiggins[27] of the

measurements by Rao, Brim and Hoffman[28] on the fundamental band of hydrogen cyanide at 800–640 cm^{-1}. Again the agreement indicates an accuracy of $\pm 0{\cdot}01$ cm^{-1}, at least for lines of small **J**-value. The calculations and measurements of Rank and co-workers on the hydrogen cyanide fundamental (3400–3200 cm^{-1}) are stated to be accurate to one part in one million, or $\pm 0{\cdot}003$ cm^{-1}.

The foregoing measurements on carbon monoxide and hydrogen cyanide probably represent the best thus far made in the region below 5000 cm^{-1}. Since they span a considerable wavenumber range in the infra-red, they represent a convenient means of establishing the absolute accuracy of infra-red measurements, either by direct comparison in the first-order or by comparison in higher orders. The fundamental of carbon monoxide is especially suitable for this purpose because of the sharpness of its lines, convenient spacing, and freedom from underlying upper-stage bands and isotope effects. It has been used for reference purposes by Rao, Brim and Hoffman[28] on hydrogen cyanide, by Rao, Ryan and Nielsen[29] on water vapour and acetylene, and by Mould, Price and Wilkinson[30] (and other work not yet published) on ammonia, hydrogen chloride and bromide, deuterium chloride and bromide, and carbon dioxide. The wavenumbers of the lines in suitable bands of these gases have thus been compared directly with those of a band of known accuracy, and many of their values established with an accuracy approaching $\pm 0{\cdot}03$ cm^{-1} or better.

On the next page the spectral ranges covered by the wavenumbers measured for the various gases are summarized, together with estimates of the absolute accuracy of the values. These measurements are of three levels of absolute accuracy: $\pm 0{\cdot}02$ or better, $\pm 0{\cdot}03$–$0{\cdot}05$, and larger than $\pm 0{\cdot}05$ cm^{-1}. In the first group are the bands of the diatomic molecules CO, HCl, HBr, DCl, plus two bands each of HCN and CO_2. These bands have all been measured against standard atomic lines or CO in at least two laboratories and the measurements have agreed to $\pm 0{\cdot}02$ cm^{-1} or better. In the second group are those in which less confidence can be placed for any of several reasons, namely, measurement in only one laboratory at high resolution, demonstrable sensitivity of the measured values to pressure effects or to spectral slit width, and disagreement between two or more laboratories to more than $\pm 0{\cdot}02$ cm^{-1}.

In the second group are combination bands of C_2H_2 and CO_2 and fundamentals of CH_4, NH_3 and N_2O. The combination bands of C_2H_2 and CO_2 have been measured in only one laboratory and those of C_2H_2 are also resolution-sensitive. The fundamentals of CH_4 and N_2O were measured in only one laboratory and are also resolution-sensitive. The widely used band of NH_3 must be assigned an accuracy no better than $\pm 0{\cdot}03$ cm^{-1} at present because of the magnitude of disagreement among the three laboratories in which this band has most recently been measured at a resolution better than $0{\cdot}1$ cm^{-1}.

Finally, the two water bands at 3700 and 1600 cm^{-1} are in a special category. These bands would be most convenient for calibration purposes because of their ubiquity, number of peaks and broad wavenumber range. Unhappily they are very sensitive to resolution and the individual lines are easily broadened by pressure. This makes both bands very difficult to

measure precisely, and also unreliable for calibration use. The band at 3700 cm^{-1} is particularly bad because of the overlapping of the two fundamentals in this region. We are therefore placing the two tables of wavenumbers for H_2O at the end of the set of tables, and are estimating the wavenumber accuracy for these bands as $\pm 0{\cdot}1$ cm^{-1}.

List of wavenumber tables, estimated precision and sources of data

Table no.	*Substance and band origin*	*Region covered by table* (cm^{-1})	*Estimated absolute accuracy* (cm^{-1})	*Sources of data*
1	CO overtone	4343–4132	±0·01	24, 25
2	C_2H_2 combination	4131–4038	±0·05	31
3	CO_2 combination	3734–3682	±0·03	32
4	CO_2 combination	3640–3579	±0·03	32
5	HCN fundamental	3386–3241	±0·01	27
6	CH_4 fundamental	3167–2936	±0·04	33
7	HCl fundamental	3060–2650	±0·02	34, 35
8	HBr fundamental	2750–2372	±0·02	34, 35
9	CO_2 fundamental	2381–2300	±0·02	33, 35
10	$^{13}CO_2$ fundamental	2295–2247	±0·02	33, 35
11	CO fundamental	2242–2013	±0·01	24, 26
12	DCl fundamental	2224–1905	±0·02	35, 36
13	DBr fundamental	1935–1727	±0·04	35, 36
14	CH_4 fundamental	1366–1248	±0·04	33
15	NH_3 fundamental	1213– 753	±0·03	30, 33, 38
16	HCN fundamental	786– 638	±0·01	27, 28
17	CO_2 fundamental	702– 629	±0·02	33, 39
18	N_2O fundamental	630– 592	±0·04	35, 36, 40
19	H_2O fundamentals*	3950–3447	±0·1	32
20	H_2O fundamental*	1890–1318	±0·1	29, 33

* The water-vapour bands are considerably inferior to the other bands listed above for calibration purposes. Unfortunately no suitable bands for the regions 4038–3734, 3579–3386, and 1727–1366 are as yet known to the Commission. This deficiency has been emphasized by placing the water-vapour bands at the end of the tables.

PROCEDURES FOR USE OF THE TABLES OF WAVENUMBERS

The two principal limitations on the accuracy with which wavenumber measurements can be made in spectrometers of moderate resolution (0·2–1 cm^{-1}) are the reproducibility of reading a specific point in a recorded spectrum (*e.g.* the position of an absorption-line maximum) and the reproducibility of the instrumental setting corresponding to a specific wavenumber. The first of these is basically set by the signal-to-noise ratio, and therefore in calibration of spectrometers the signal-to-noise ratio should be as high as possible (see p. 558). The instrumental setting is indicated in different ways by drum numbers, scale readings, pip numbers and so on, which are related to the setting of the grating or Littrow mirror. The reproducibility of the instrumental setting can be measured by repeated running of the same sharp-lined spectrum at high signal-to-noise ratio and slow scanning rate, and observing the magnitude of apparent changes in positions of the line maxima.

There are several procedures for calibrating the instrumental setting, as indicated by its scale reading, in terms of vacuum wavenumbers. These are the calibration-curve method, the interpolation method and the superposition method.

The calibration curve method

In this method the spectra of calibrating gases are obtained and the scale readings corresponding to their absorption maxima are determined. A large-scale smooth curve is then plotted with the standard vacuum wavenumbers of the maxima taken from the tables as ordinates and the scale readings of the maxima as abscissa. Wavenumbers of maxima or other desired points in unknown spectra are then determined by measurement of their scale readings and subsequent conversion to wavenumbers by reading them from the calibration curve. This procedure is rapid and simple. Its accuracy is limited by the stability of the instrument over the period of time during which the curve is assumed correct.

Interpolation method

The spectra of the calibrating gas or gases and that of the unknown are run in succession. The scale readings of the unknown are converted to vacuum wavenumbers by interpolation between the known wavenumbers of the calibrating gas. Interpolation can be linear if the spacing of the known absorption maxima is not too large or the desired accuracy is not high. The linearity can be checked by plotting a calibration curve. For non-linear interpolation, a procedure such as that proposed by McKinney and Friedel[41], Downie *et al.*[42], and Bethke[43] may be followed. For the highest precision in interpolation, interference fringes may be used[15] though these would rarely be necessary if an accuracy no higher than $\pm 0{\cdot}03\ cm^{-1}$ is wanted.

Superposition method

Many sources of error are eliminated or minimized by simultaneous recording of the unknown and calibration spectra. This can be done by placing two absorption cells in series. The two spectra can then be recorded as one and the interpolation procedures followed. In any event, the light path followed by the radiation should be the same for both the unknown and the calibrating gas.

Other factors which must be controlled during precise wavenumber measurement are:

Refractive index of the atmosphere in the spectrometer—The following tables give the wavenumbers in cm^{-1} *in vacuo* for the absorption maxima. If the atmosphere in the spectrometer is approximately the same as to pressure, temperature and humidity when the spectra of the unknown and the calibrating gas are recorded, the interpolated wavenumbers for the unknown will also be the values *in vacuo*. However, if the atmospheric conditions change markedly, or if the spectrum of the calibrating gas is obtained in a different grating order from that used for the unknown, appropriate correction must be made. Equations for correcting for barometric pressure and temperature are given on pp. 549 and 553 and the method for correcting for grating orders is as follows:

To compute wavenumbers *in vacuo*, ν_u vac., for an unknown (u), whose spectrum is observed in grating order M_u and in a wavenumber region where the refractive index of air is n_u, it is first necessary to correct the tabulated wavenumbers in vacuo, ν_c vac., of the calibrating gas whose spectrum is recorded in grating order M_c at the wavenumber region where the refractive index of air is n_c. The correction factor by which ν_c vac. is multiplied is $n_c M_u / n_u M_c$. If the unknown and calibration spectra are observed in the same wavenumber region, of course the refractive indices n_c and n_u are the same, and the grating orders would also be the same. The correction factor then reduces to unity.

Pressure effects on wavenumber measurement in spectra of gases—There are several pressure effects of foremost importance when high wavenumber accuracy is sought. These are pressure broadening, pressure effects on line asymmetry and pressure-induced displacement of the absorption maximum. Pressure broadening is the most important of these because the magnitude of the broadening (of the order of 0·1 to 0·3 cm^{-1} per atmosphere) approaches the spectral slit widths of spectrometers of intermediate resolution. Thus two lines observed at low pressure (say 10 mm) might have half-widths of 0·05 cm^{-1} and a readily resolvable separation of 0·5 cm^{-1}. In the presence of an inert gas at 1 atm pressure, however, the half-widths might rise to 0·3 cm^{-1} and make it quite difficult for the spectrometer to separate them. Even more important, their maxima would be drawn closer together and the apparent wavenumbers of the maxima would be in error by 0·1 cm^{-1} or perhaps more. This effort is observable for many lines in the spectrum of water vapour obtained with atmospheric moisture, and makes such lines unsuitable for calibrating use if accuracy better than $\pm 0{\cdot}1$ cm^{-1} is wanted.

When a line is asymmetric, two effects will occur if the line is observed at high pressure. The shape of the line may be changed by the pressure, which will cause a shift in the wavenumber of the maximum, and the line may be observed at too high a value of the peak absorbance, which will tend to flatten the peak and mislead the experimenter in his attempt to locate the maximum. The usual cause of line asymmetry is the superposition of several unresolved components. Such lines are poor choices for wavenumber standards, and have been avoided so far as possible in the following tables.

It can be shown on theoretical grounds, and also verified experimentally, that pressure shifts the position of a line maximum. Fortunately, at pressures of one atmosphere or less, this effect is small and need not be of concern for limits of error larger than $\pm 0{\cdot}01$ cm^{-1}.

Temperature effects—These may be divided into the effects of temperature on the spectrum and those on the instrumentation. The latter are more serious but will not be considered. Temperature can broaden lines through the Doppler effect but this is unimportant for present purposes since the broadening at room temperature for light molecules is about 0·01 cm^{-1} and is less for heavy ones. Temperature can increase vapour pressure of high-boiling liquids so that the amount of gas in an absorption cell could be strongly temperature-dependent if it is temperature-limited. The intensity of difference bands varies strongly with temperature, and if these are of appreciable intensity compared with the lines of an overlapping fundamental, the wavenumbers of the latter can be affected. This is not believed to be a serious

factor in any of the bands listed in these tables and if the calibrating gases are used within 5° of the stated temperature of 25°C, no effect on wavenumber accuracy should be observable.

Electronic and mechanical effects—As was mentioned on p. 19, signal-to-noise ratio sets a basic limitation on the precision with which an absorption maximum can be located on the wavenumber scale. A spectrum on which accurate wavenumber measurements are to be made should therefore be recorded with as high a signal-to-noise ratio as can be obtained under the desired conditions of resolution and scanning time. The ratio should not be less than 30:1 and if possible should be much larger.

Since most spectra are now recorded automatically, the speed of recording is an important factor. Rate of recording should be slow enough so that the entire detecting, amplifying and recording system has time to reach a high fraction (say 99 per cent) of the recorded response which would be reached in an indefinitely long time. This requirement is particularly important for the sharp lines used for calibration purposes. The spectrum should also be recorded in the same direction for the calibrating gas and the unknown, and this should be the direction of smoothest wavenumber scan, as determined by the design of the driving mechanism.

TABLES OF WAVENUMBERS

The following twenty tables are illustrated by spectra obtained with a small grating spectrometer. The gaseous samples were contained in cells 10 cm long (except for *Tables 19* and *20*), at suitable pressures as indicated in the footnote to each table. These conditions refer to those under which the illustrations were obtained, and not to those used by investigators cited in the footnotes. The percentage absorption in arbitrary units is plotted upwards, and the wavenumbers in cm^{-1} are shown increasing to the left. The wavenumber scale is non-linear and is placed on the figures for convenience only. It is not intended to be an accurate scale, since the precise wavenumbers of the identified lines may be read from the adjacent table. The numbering of the lines is for identification purposes and bears no relationship to rotational quantum numbers. Occasionally, for clarity in lettering, numbers have been systematically omitted. There should be no difficulty assigning the omitted numbers to the correct lines. The chemical formula of each gas is given on its spectrum. Wavenumber values marked* in the tables are believed to be less reliable than the other values for calibration purposes because of their resolution-sensitivity, dependence on pressure or other complications.

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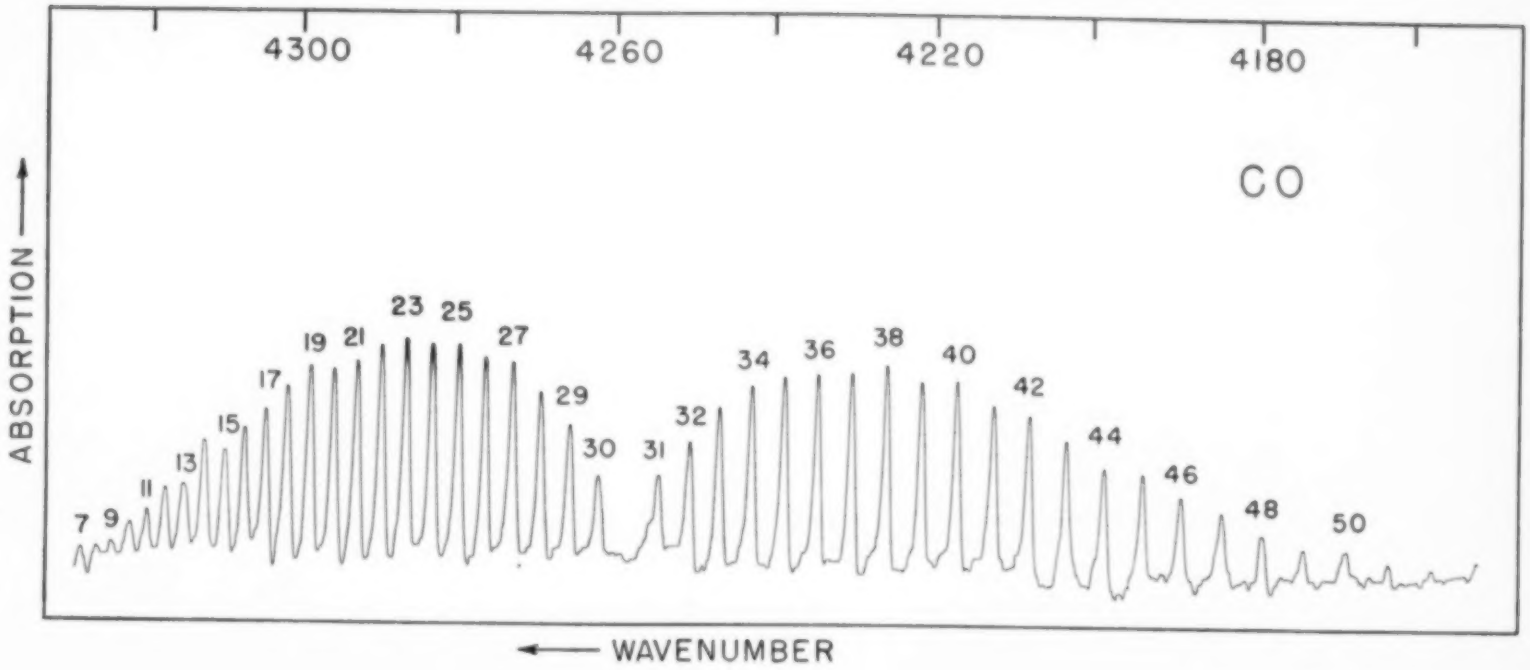
4300
4260
4220
4180
CO
ABSORPTION
WAVENUMBER
7
9
11
13
15
17
19
21
23
25
27
29
30
31
32
34
36
38
40
42
44
46
48
50

560

Table 1. Carbon monoxide overtone band: 4343–4132 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	4342·20	21	$4294{\cdot}64_0$	41	$4213{\cdot}96_2$
2	4340·52	22	$4291{\cdot}50_6$	42	$4209{\cdot}35_6$
3	4338·76	23	$4288{\cdot}29_4$	43	$4204{\cdot}67_3$
4	4336·93	24	$4285{\cdot}01_2$	44	$4199{\cdot}93_1$
5	4335·03	25	$4281{\cdot}65_8$	45	$4195{\cdot}12_0$
6	$4333{\cdot}05_5$	26	$4278{\cdot}23_5$	46	$4190{\cdot}23_8$
7	4331·02	27	$4274{\cdot}74_7$	47	$4185{\cdot}30_0$
8	4328·88	28	$4271{\cdot}18_1$	48	$4180{\cdot}28_6$
9	4326·70	29	$4267{\cdot}54_8$	49	$4175{\cdot}20_8$
10	4324·42	30	$4263{\cdot}84_0$	50	$4170{\cdot}06_2$
11	$4322{\cdot}07_3$	31	$4256{\cdot}22_6$	51	$4164{\cdot}85_2$
12	$4319{\cdot}65_9$	32	$4252{\cdot}30_8$	52	$4159{\cdot}56_4$
13	$4317{\cdot}16_7$	33	$4248{\cdot}33_0$	53	$4154{\cdot}23_4$
14	$4314{\cdot}60_2$	34	$4244{\cdot}27_3$	54	$4148{\cdot}81_7$
15	$4311{\cdot}96_6$	35	$4240{\cdot}15_0$	55	4143·33
16	$4309{\cdot}26_0$	36	$4235{\cdot}95_0$	56	4137·78
17	$4306{\cdot}48_2$	37	$4231{\cdot}69_0$	57	4132·18
18	$4303{\cdot}61_4$	38	$4227{\cdot}37_1$		
19	$4300{\cdot}71_2$	39	$4222{\cdot}96_4$		
20	$4297{\cdot}70_2$	40	$4218{\cdot}50_3$		

Data from Plyler, Allen and Tidwell[25] and Rank, Guenther, Saksena, Shearer and Wiggins[24]. Cell length, 10 cm, p = 500 mm, t = 25°C, approximate spectral slit width, 1·1 cm^{-1}. The accuracy of these lines is ±0·01 cm^{-1}, and the precision somewhat better.

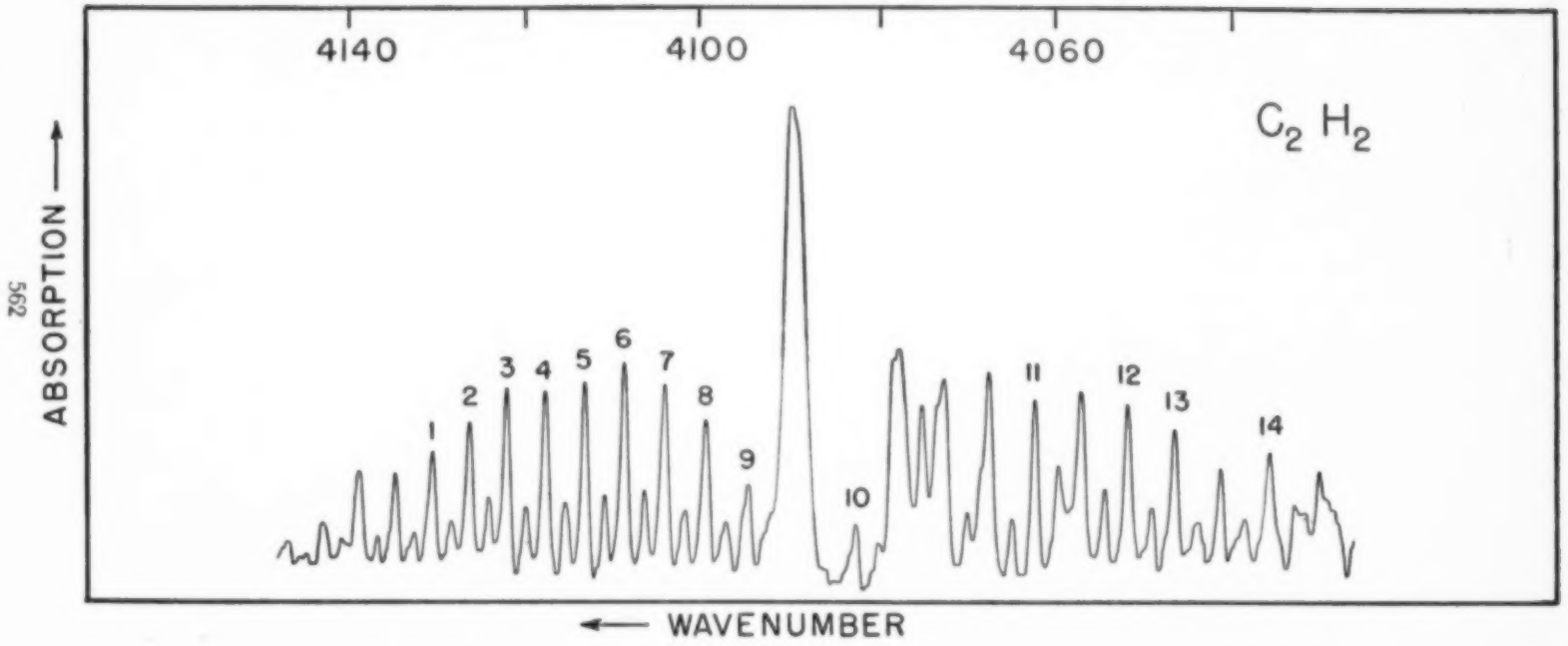
4140
4100
4060
$C_2 H_2$
ABSORPTION
WAVENUMBER
1
2
3
4
5
6
7
8
9
10
11
12
13
14

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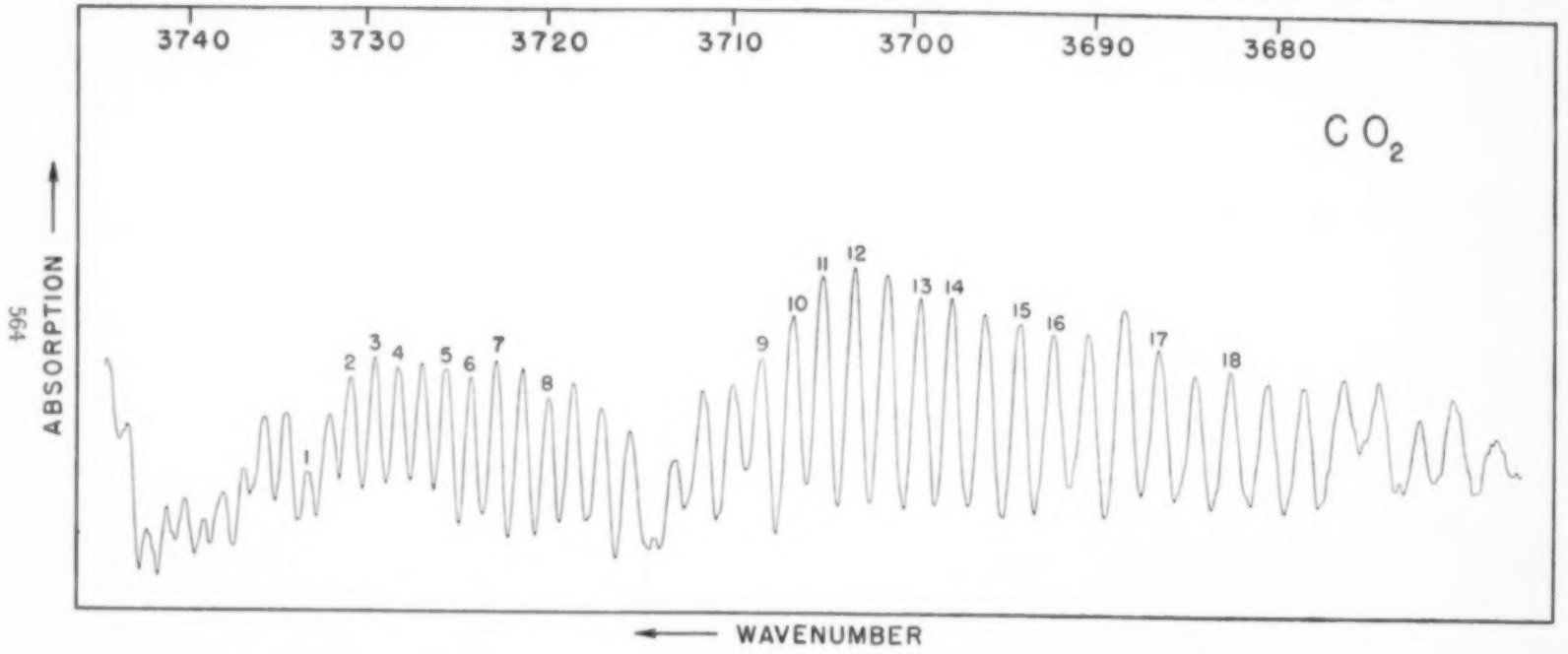
Table 2. Acetylene combination band: 4131–4038 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	4130·10	8	4100·47
2	4126·91	9	4095·84
3	4122·63	10	4084·14
4	4118·30	11	4064·58
5	4113·94	12	4054·52
6	4109·47	13	4049·36
7	4104·98*	14	4038·95

Data from Allen, Plyler and Tidwell[31]. In view of the pressure-dependence and resolution-sensitivity of this band, and of the fact that it has been measured in only one laboratory in recent years, the wavenumbers of *Table 2* are provisionally assigned a precision of $\pm 0{\cdot}03$ cm^{-1}. Their accuracy is believed to be within $\pm 0{\cdot}05$ cm^{-1}. Cell length, 10 cm, $p = 760$ mm, $t \approx 25°C$, approximate spectral slit width, $0{\cdot}9$ cm^{-1}.


3740
3730
3720
3710
3700
3690
3680
CO_2
ABSORPTION
WAVENUMBER
1
2
3
4
5
6
7
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11
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16
17
18

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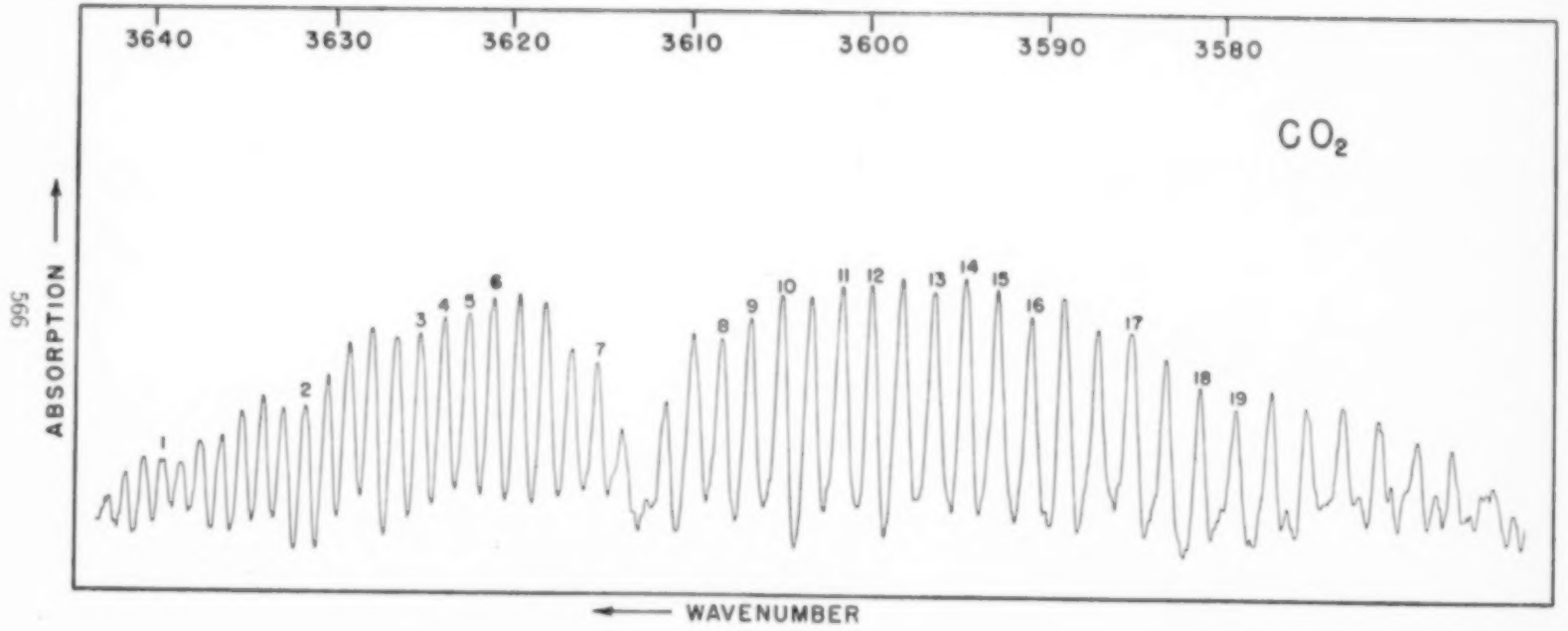
Table 3. Carbon dioxide combination band: 3734–3682 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	3733·48	10	3706·70
2	3731·01	11	3705·02
3	3729·73	12	3703·29
4	3728·42	13	3699·79
5	3725·72*	14	3698·00
6	3724·35	15	3694·34*
7	3722·90	16	3692·46
8	3720·09	17	3686·74
9	3708·38	18	3682·78

Data from Plyler and Tidwell[32]. These values have been compared with those of Courtoy[44], and are regularly about 0·06 cm^{-1} higher. However, Courtoy subtracted a relatively large correction (0·1–0·2 cm^{-1}) from his measured numbers because the optical path of his interferometer beam through the spectrometer was different from that of the radiation being measured. This correction was determined by theory and apparently was not checked against a precisely known set of absorption lines. In view of this, the values of Courtoy have not been averaged with those of Plyler and Tidwell, but the latter are taken as correct within ±0·03 cm^{-1}. Cell length, 10 cm, p = 200 mm, t = 25°C, approximate spectral slit width, 0·9 cm^{-1}.


3640
3630
3620
3610
3600
3590
3580
CO_2
ABSORPTION
WAVENUMBER
1
2
3
4
5
6
7
8
9
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11
12
13
14
15
16
17
18
19

VOL.
1
1960

Table 4. Carbon dioxide combination band: 3640–3579 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	3640·00*	11	3601·40*
2	3631·85	12	3599·74*
3	3625·27	13	3596·22
4	3623·93	14	3594·42
5	3622·50	15	3592·65*
6	3621·17*	16	3590·78
7	3615·25*	17	3585·21
8	3608·07	18	3581·31
9	3606·48	19	3579·34
10	3604·81		

Data from Plyler and Tidwell[28]. These values have been compared with those of Courtoy[44], and are regularly about 0·06 cm^{-1} higher. However, Courtoy subtracted a relatively large correction (0·1–0·2 cm^{-1}) from his measured numbers because the optical path of his interferometer beam through the spectrometer was different from that of the radiation being measured. This correction was determined by theory and apparently was not checked against a precisely known set of absorption lines. In view of this, the values of Courtoy have not been averaged with those of Plyler and Tidwell, but the latter are taken as correct within ±0·03 cm^{-1}. Cell length, 10 cm, p = 200 mm, t = 25°C, approximate spectral slit width, 0·9 cm^{-1}.

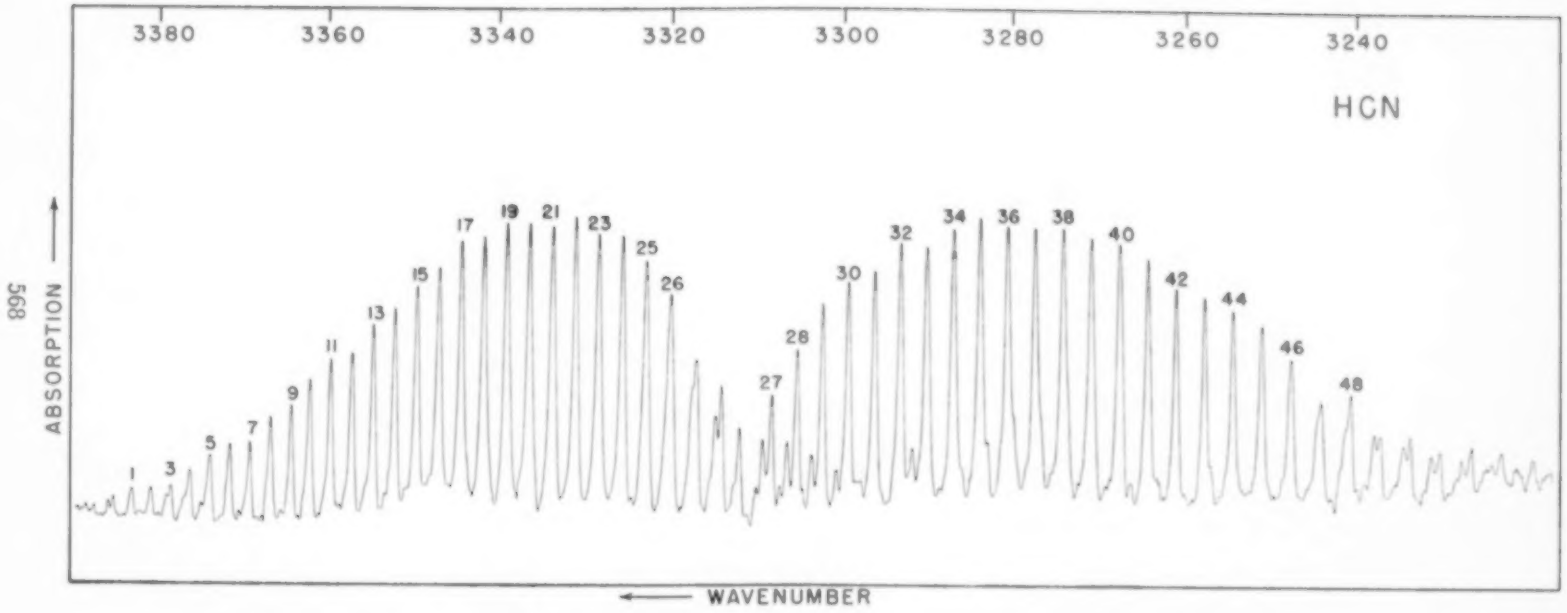
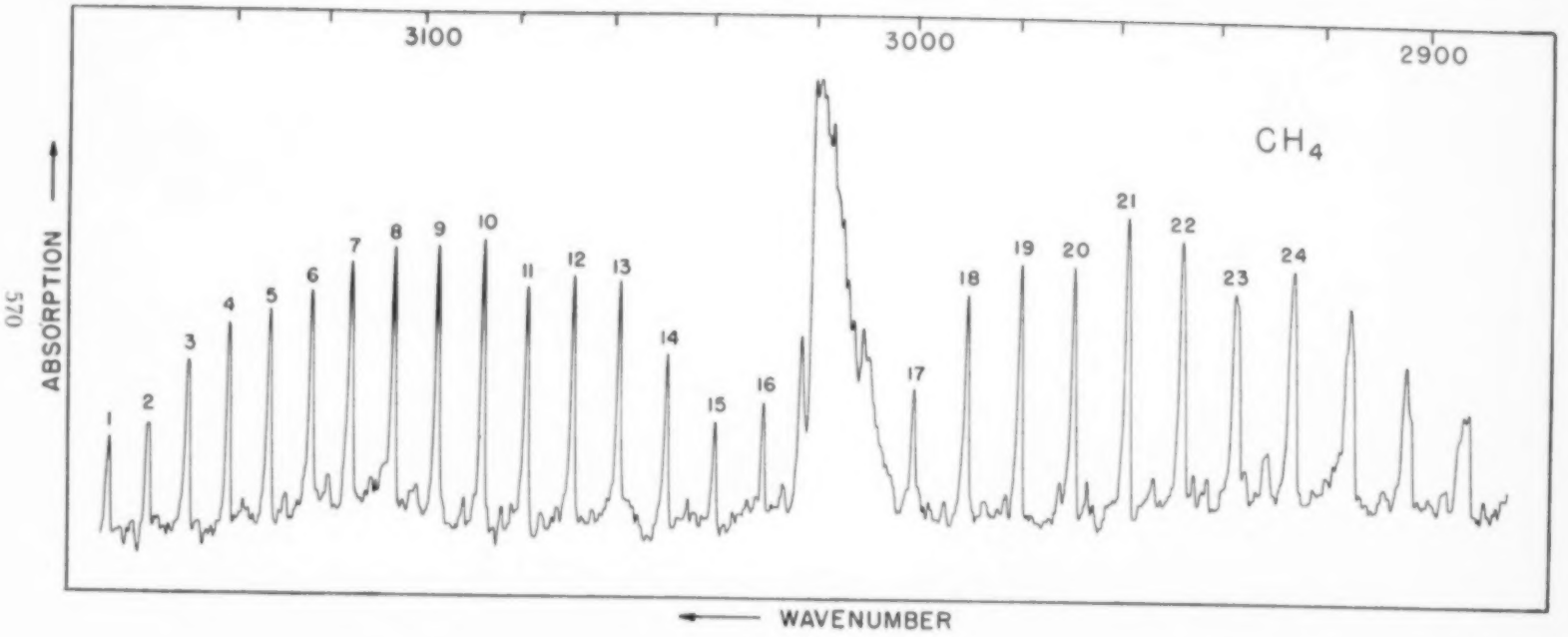

3380
3360
3340
3320
3300
3280
3260
3240
HCN
ABSORPTION
568
1
3
5
7
9
11
13
15
17
19
21
23
25
26
27
28
30
32
34
36
38
40
42
44
46
48
WAVENUMBER

Table 5. Hydrogen cyanide fundamental: 3386–3241 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	3385·55	17	3345·31	33	3290·34
2	3383·20	18	3342·60	34	3287·24
3	3380·83*	19	3339·88	35	3284·12
4	3378·44	20	3337·14	36	3280·98
5	3376·02	21	3334·37	37	3277·82
6	3373·59	22	3331·58	38	3274·64
7	3371·12	23	3328·77	39	3271·44
8	3368·64	24	3325·94	40	3268·22
9	3366·14	25	3323·09	41	3264·98
10	3363·61	26	3320·22	42	3261·72
11	3361·06	27	3308·52*	43	3258·44
12	3358·49	28	3305·54	44	3255·14
13	3355·90	29	3302·54	45	3251·82
14	3353·28	30	3299·52	46	3248·48
15	3350·64	31	3296·48	47	3245·12*
16	3347·99	32	3293·42	48	3241·75*

Data from Rank, Skorinko, Eastman and Wiggins[37]. These numbers are comparable in accuracy and precision to those of *Table 1*. According to these authors, the values of *Table 5*, which are smoothed values that have been checked at various lines and agree to $\pm 0{\cdot}003$ cm^{-1} or better, are relatively precise to one part in 10^7 and accurate to 3 parts in 10^7. For measurements at intermediate resolution they may be relied on to $\pm 0{\cdot}01$ cm^{-1}. Cell length, 10 cm, $p = 20$ mm, $t = 25°C$, approximate spectral slit width, 0·65 cm^{-1}.


3100
3000
2900
CH_4
ABSORPTION
WAVENUMBER
1
2
3
4
5
6
7
8
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10
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12
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Table 6. Methane fundamental: 3167–2926 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	3166·20	13	3057·79
2	3157·61	14	3048·25
3	3148·95	15	3038·58
4	3140·20	16	3028·84
5	3131·39	17	2999·10
6	3122·46	18	2988·97*
7	3113·42	19	2979·00
8	3104·36	20	2968·67
9	3095·22	21	2958·20
10	3086·02	22	2947·92
11	3076·74	23	2937·34*
12	3067·30	24	2926·86*

Data from Plyler, Danti, Blaine and Tidwell[33]. Many of the lines of this band are resolution-sensitive, but some standard is needed to bridge the large gap between the upper lines of the hydrogen chloride fundamental and the lower frequencies of *Table 5*, which the methane fundamental does in part. Because recent high-precision work on this band has been published from only one laboratory and because of the unsatisfactory nature of many of these lines as standards, the accuracy of the values in *Table 6* is taken to be $\pm 0{\cdot}04$ cm^{-1}. Cell length, 10 cm, $p = 60$ mm, $t = 25°C$, approximate spectral slit width, 0·65 cm^{-1}.

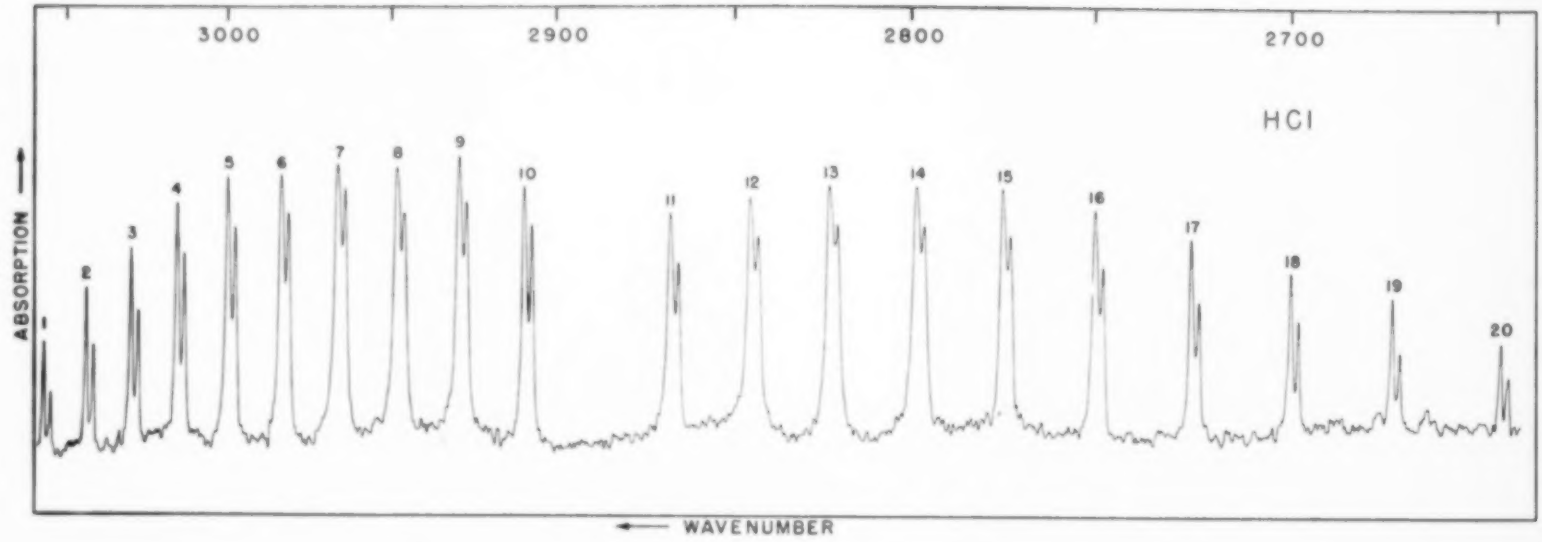
3000
2900
2800
2700
HCl
ABSORPTION
WAVENUMBER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

Table 7. Hydrogen chloride fundamental: 3060–2650 cm^{-1}

Line pair no.	*Wavenumber* (vac.) (cm^{-1}) $H^{35}Cl$	$H^{37}Cl$	*Line pair no.*	*Wavenumber* (vac.) (cm^{-1}) $H^{35}Cl$	$H^{37}Cl$
1	3059·32	3056·97	11	2865·10	2863·02
2	3045·06	3042·73	12	2843·62	2841·58
3	3030·09	3027·78	13	2821·56	2819·56
4	3014·41	3012·12	14	2798·94	2796·97
5	2998·04	2995·78	15	2775·76	2773·82
6	2981·00	2978·75	16	2752·04	2750·13
7	2963·29	2961·07	17	2727·78	2725·92
8	2944·90	2942·72	18	2703·01	2701·18
9	2925·90	2923·72	19	2677·73	2675·94
10	2906·24	2904·11	20	2651·96	2650·22

Data are from Plyler and Tidwell[34] and Mould, Price and Wilkinson[35]. The agreement of these two laboratories is very close. The relative precision is $\pm 0{\cdot}01$ cm^{-1} and the accuracy $\pm 0{\cdot}02$ cm^{-1}. Cell length, 10 cm, $p = 250$ mm, $t = 25°C$, approximate spectral slit width, 0·7 cm^{-1}.

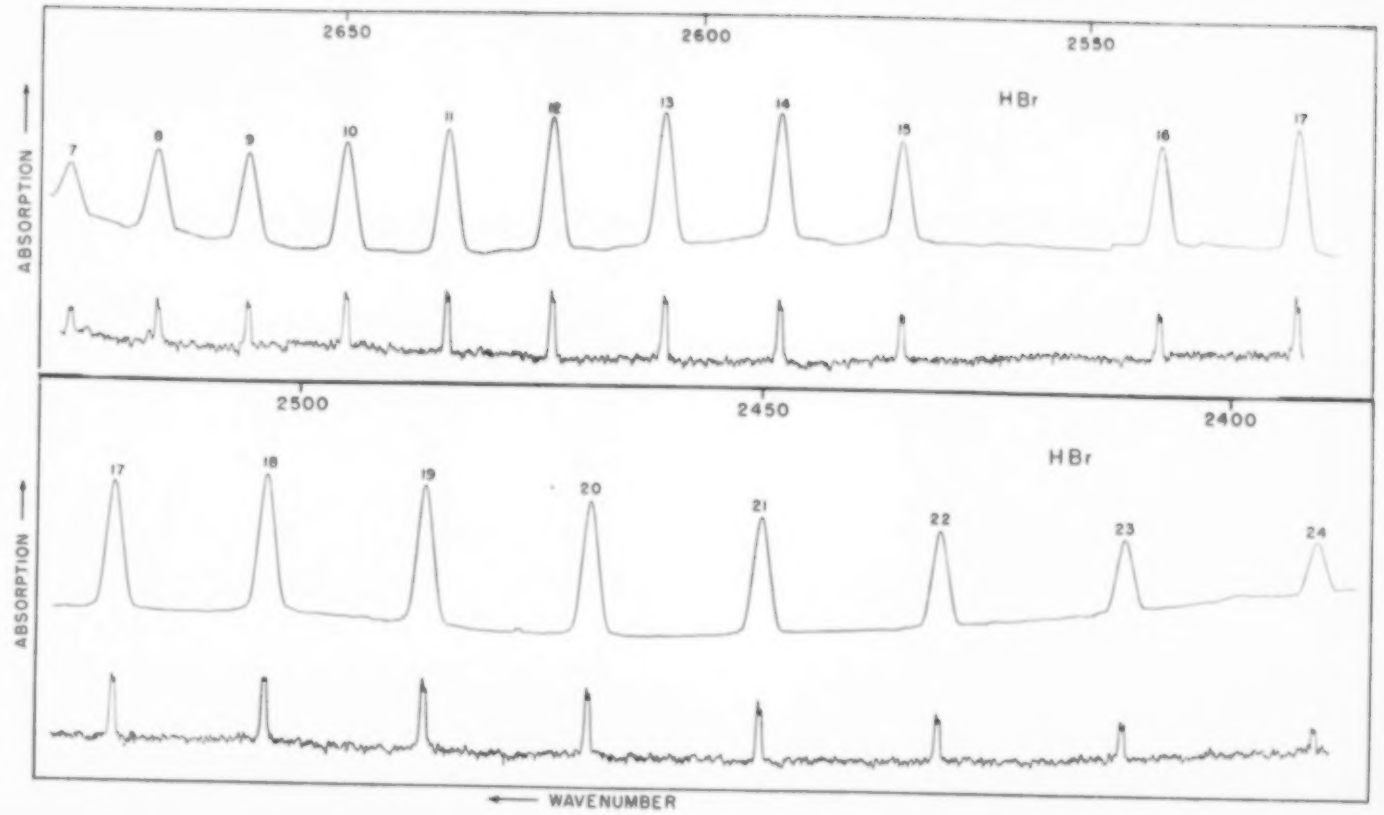
2650
2600
2550
HBr
7
8
9
10
11
12
13
14
15
16
17
ABSORPTION
2500
2450
2400
HBr
17
18
19
20
21
22
23
24
ABSORPTION
WAVENUMBER

Table 8. Hydrogen bromide fundamental: 2750–2372 cm^{-1}

Line pair no.	*Wavenumber* (vac.) (cm^{-1}) $H^{79}Br$	$H^{81}Br$	*av.*	*Line pair no.*	*Wavenumber* (vac.) (cm^{-1}) $H^{79}Br$	$H^{81}Br$	*av.*
1	2749·33	2748·90	2749·12	16	2542·25	2541·87	2542·06
2	2740·42	2739·98	2740·20	17	2525·09	2524·72	2524·91
3	2730·93	2730·49	2730·71	18	2507·48	2507·12	2507·30
4	2720·87	2720·44	2720·66	19	2489·43	2489·08	2489·26
5	2710·26	2709·84	2710·05	20	2470·96	2470·61	2470·79
6	2699·10	2698·68	2698·89	21	2452·07	2451·72	2451·90
7	2687·40	2686·97	2687·19	22	2432·76	2432·42	2432·59
8	2675·16	2674·74	2674·95	23	2413·06	2412·72	2412·89
9	2662·40	2661·98	2662·19	24	2392·96	2392·63	2392·80
10	2649·12	2648·71	2648·92	25	2372·45	2372·13	2372·29
11	2635·32	2634·92	2635·12				
12	2621·02	2620·62	2620·82				
13	2606·23	2605·83	2606·03				
14	2590·95	2590·56	2590·76				
15	2575·19	2574·80	2575·00				

Data are from Plyler and Tidwell[36] and Mould, Price and Wilkinson[35]. The agreement between the two sets of data is very close. The relative precision is $\pm 0{\cdot}01$ cm^{-1} and the accuracy $\pm 0{\cdot}02$ cm^{-1}. A study by Plyler, Danti, Blaine and Tidwell[35] shows that for spectrometers of insufficient resolving power to separate the $H^{79}Br$—$H^{81}Br$ doublet cleanly, the measured centre of gravity of the doublet is given within the accuracy of the measurement by the average of the high-resolution values for the components. This average is therefore included in *Table 8*. Cell length, 10 cm, p = 60 and 140 mm, t = 25°C, approximate spectral slit width, 0·5 and 0·8 cm^{-1}.

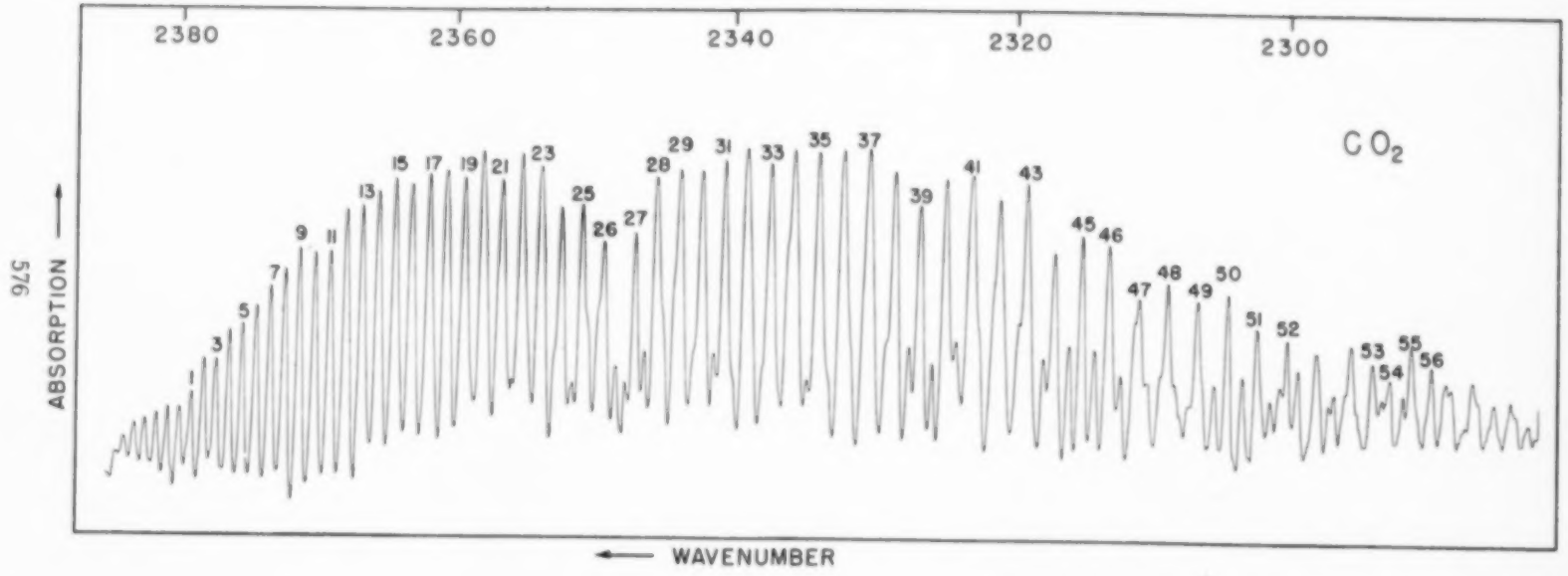
2380
2360
2340
2320
2300
CO_2
ABSORPTION
WAVENUMBER
1
3
5
7
9
11
13
15
17
19
21
23
25
26
27
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Table 9. Carbon dioxide fundamental: 2381–2300 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	2380·74	21	2357·37	41	2323·10
2	2379·80	22	2355·94	42	2321·16
3	2378·86	23	2354·48	43	2319·20
4	2377·88	24	2353·00*	44	2317·22
5	2376·87	25	2351·50*	45	2315·21
6	2375·83	26	2349·96*	46	2313·18
7	2374·79	27	2347·62*	47	2311·12
8	2372·70	28	2346·03*	48	2309·05
9	2373·61	29	2344·41*	49	2306·95
10	2371·47	30	2342·77	50	2304·84
11	2370·32	31	2341·11	51	2302·69
12	2369·12	32	2339·42	52	2300·50*
13	2367·92	33	2337·70		
14	2366·69	34	2335·96*	53	2294·45*
15	2365·41	35	2334·19	54	2293·10*
16	2364·15	36	2332·40	55	2291·62*
17	2362·85	37	2330·59	56	2290·23
18	2361·51	38	2328·76*		(Lines 53–56 from carbon-13 dioxide)
19	2360·16	39	2326·90		
20	2358·77	40	2325·01		

Data from Plyler, Danti, Blaine and Tidwell[29] and Mould, Price and Wilkinson[35]. The measurements agree to better than ±0·02. The values of Mould, Price and Wilkinson were smoothed values. It is estimated that the precision is ±0·01 cm^{-1} and the absolute accuracy is ±0·02 cm^{-1} except for the starred lines. Cell length, 10 cm, p = 30 mm, t = 25°C, approximate spectral slit width, 0·5 cm^{-1}.

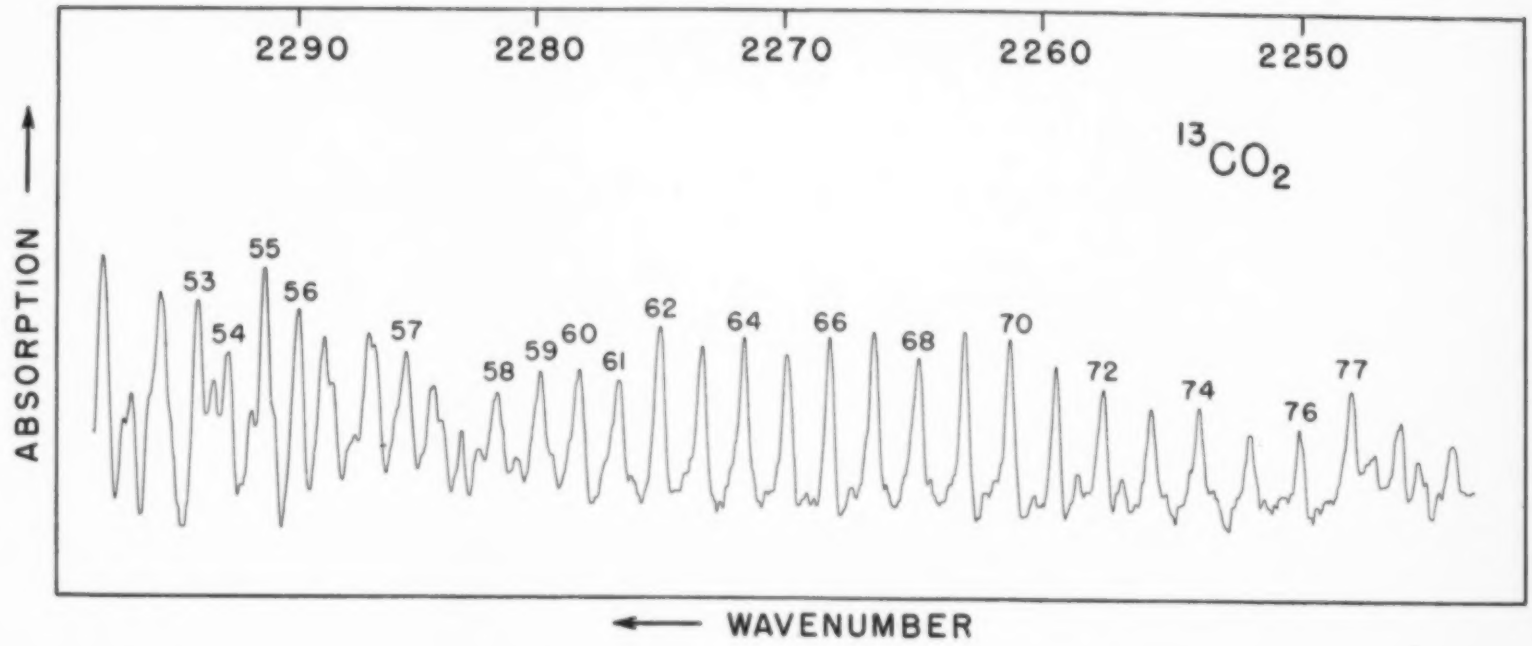
2290
2280
2270
2260
2250
$^{13}CO_2$
ABSORPTION
53
54
55
56
57
58
59
60
61
62
64
66
68
70
72
74
76
77
WAVENUMBER

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Table 10. Carbon-13 dioxide fundamental: 2295–2247 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
53	2294·45*	66	2268·55
54	2293·10*	67	2266·76
55	2291·62*	68	2264·96
56	2290·23	69	2263·14
57	2285·79*	70	2261·29
58	2281·93*	71	2259·42
59	2280·33	72	2257·52
60	2278·71	73	2255·60
61	2277·09	74	2253·66
62	2275·42	75	2251·69
63	2273·74	76	2249·68
64	2272·03	77	2247·68
65	2270·30		

Data from Plyler, Danti, Blaine and Tidwell[33] and Mould, Price and Wilkinson[38]. The measurements agree to better than ±0·02. The values of Mould, Price and Wilkinson were smoothed values. It is estimated that the precision is ±0·01 cm^{-1} and the absolute accuracy is ±0·02 cm^{-1} except for the starred lines. Cell length, 10 cm, p = 50 mm, t = 25°C, approximate spectral slit width, 0·5 cm^{-1}.

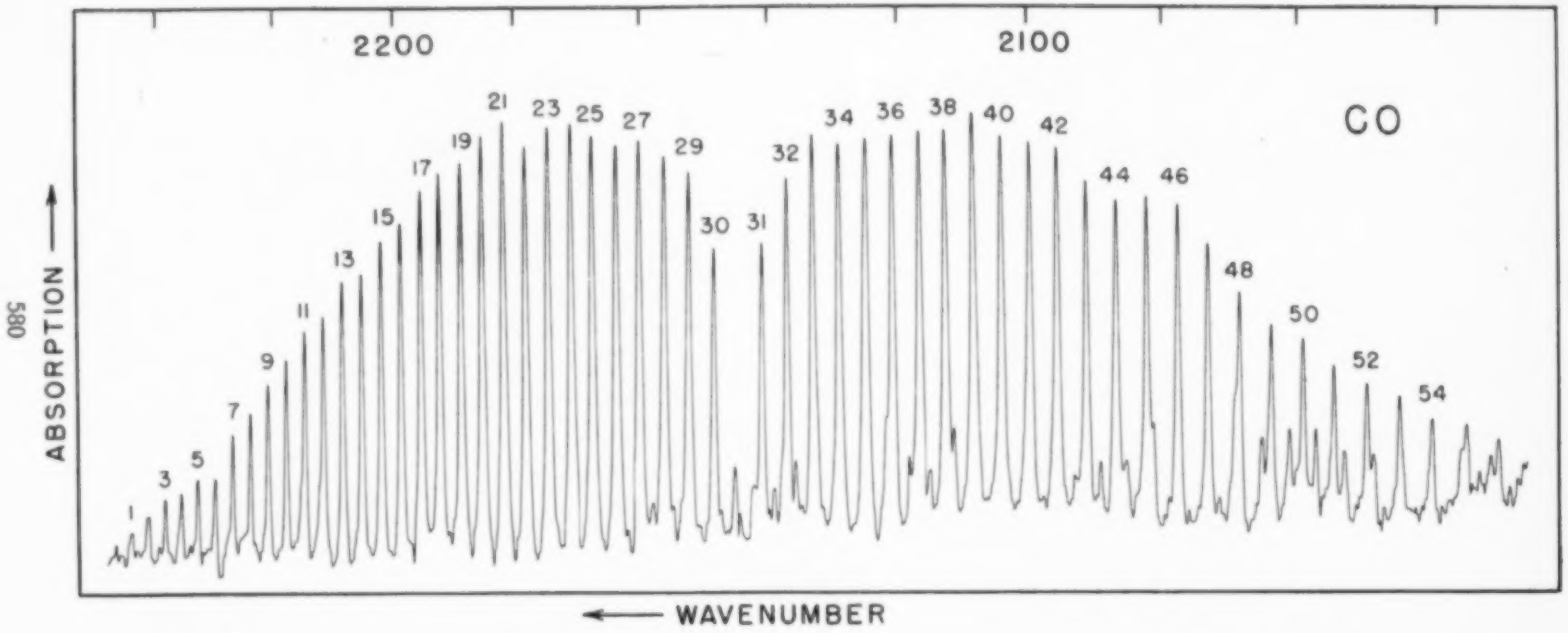
2200
2100
CO
ABSORPTION
580
WAVENUMBER
3
5
7
9
11
13
15
17
19
21
23
25
27
29
30
31
32
34
36
38
40
42
44
46
48
50
52
54

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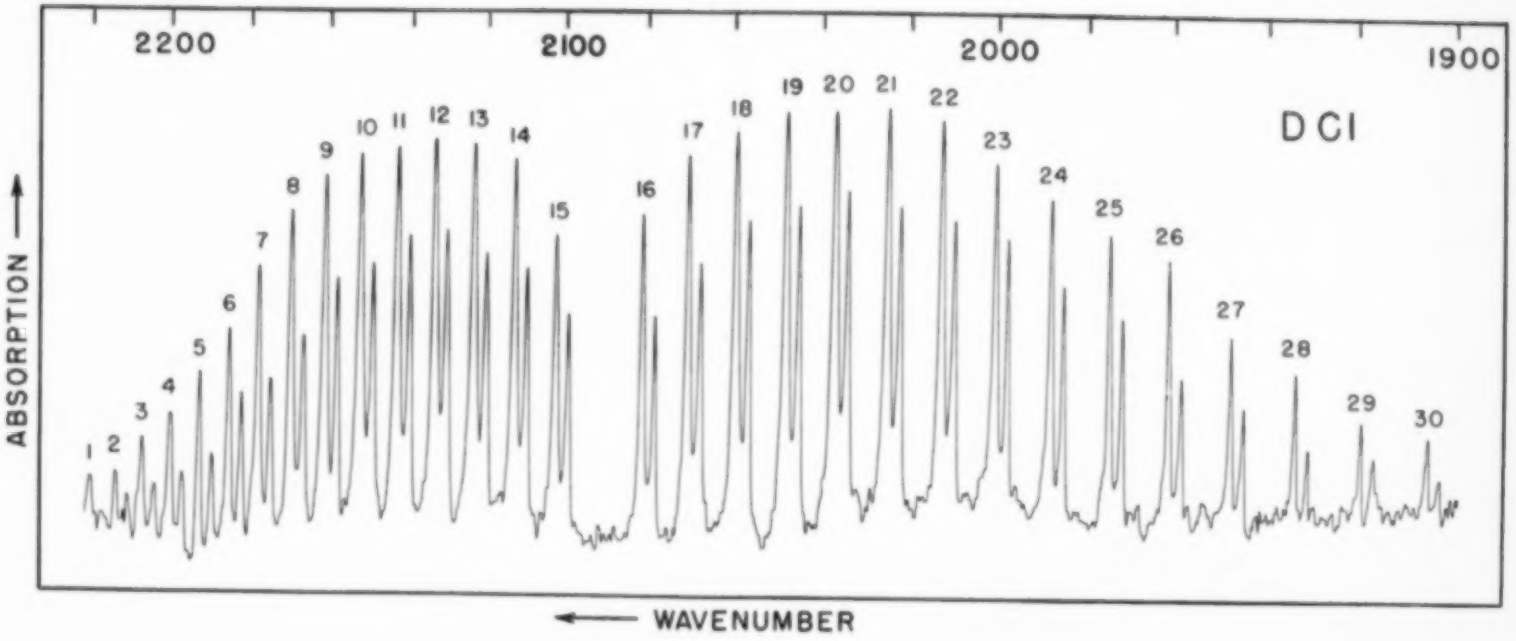
Table 11. Carbon monoxide fundamental: 2242–2013 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	$2241{\cdot}68_5$	21	$2179{\cdot}77_0$	41	$2099{\cdot}09_0$
2	$2238{\cdot}95_8$	22	$2176{\cdot}28_8$	42	$2094{\cdot}86_6$
3	$2236{\cdot}18_8$	23	$2172{\cdot}76_0$	43	$2090{\cdot}61_0$
4	$2233{\cdot}36_2$	24	$2169{\cdot}20_0$	44	$2086{\cdot}32_3$
5	$2230{\cdot}52_4$	25	$2165{\cdot}60_4$	45	$2082{\cdot}00_6$
6	$2227{\cdot}63_8$	26	$2161{\cdot}97_1$	46	$2077{\cdot}65_1$
7	$2224{\cdot}71_2$	27	$2158{\cdot}30_5$	47	$2073{\cdot}26_5$
8	$2221{\cdot}75_0$	28	$2154{\cdot}59_8$	48	$2068{\cdot}85_0$
9	$2218{\cdot}74_6$	29	$2150{\cdot}86_0$	49	$2064{\cdot}39_7$
10	$2215{\cdot}70_5$	30	$2147{\cdot}08_5$	50	$2059{\cdot}91_3$
11	$2212{\cdot}62_4$	31	$2139{\cdot}43_0$	51	$2055{\cdot}40_0$
12	$2209{\cdot}51_0$	32	$2135{\cdot}55_0$	52	$2050{\cdot}85_5$
13	$2206{\cdot}35_4$	33	$2131{\cdot}63_5$	53	$2046{\cdot}27_8$
14	$2203{\cdot}16_0$	34	$2127{\cdot}68_8$	54	$2041{\cdot}66_3$
15	$2199{\cdot}93_3$	35	$2123{\cdot}70_2$	55	$2037{\cdot}03_0$
16	$2196{\cdot}66_4$	36	$2119{\cdot}68_4$	56	$2032{\cdot}35_3$
17	$2193{\cdot}36_0$	37	$2115{\cdot}63_2$	57	$2027{\cdot}65_0$
18	$2190{\cdot}02_0$	38	$2111{\cdot}55_0$	58	$2022{\cdot}91_0$
19	$2186{\cdot}64_0$	39	$2107{\cdot}42_8$	59	2018·15
20	$2183{\cdot}22_8$	40	$2103{\cdot}27_0$	60	2013·35

Data are from Plyler, Blaine and Connor[25], and the calculations of Rank and co-workers[24]. These two sets of values agree so closely that small errors due to optical displacement of standard and sample, lack of coincidences between orders, and uncertainty in the refractive index of air appear to have been reduced well below 0·01 cm^{-1}. Because of the sharpness and convenient spacing of the lines and freedom from underlying bands, this band is an excellent reference standard for assessment of the absolute accuracy of infra-red wavenumbers measured in absorption in gases. The values listed are considered reliable to $\pm 0{\cdot}01$ cm^{-1} in absolute accuracy. Cell length, 10 cm, $p = 150$ mm, $t = 25°C$, approximate spectral slit width, 0·45 cm^{-1}.


2200
2100
2000
1900
DCl
ABSORPTION
WAVENUMBER
1
2
3
4
5
6
7
8
9
10
11
12
13
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15
16
17
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19
20
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27
28
29
30

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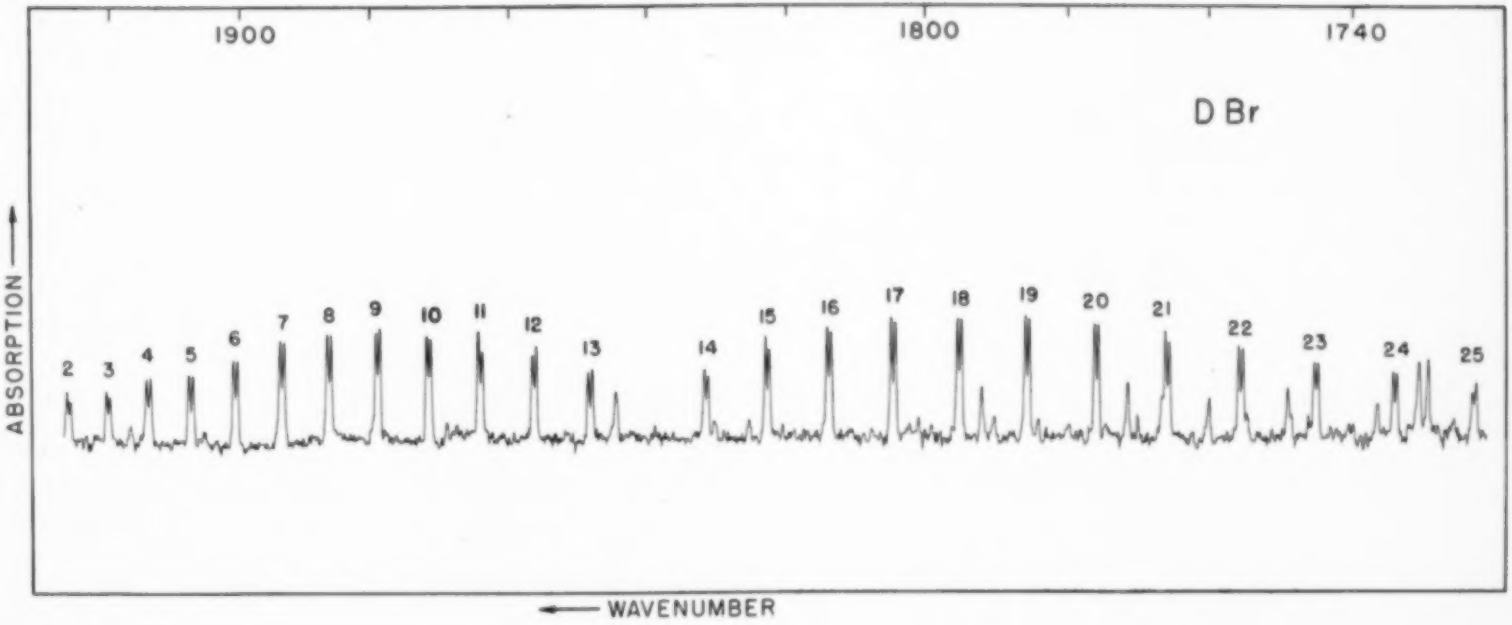
1960

Table 12. Deuterium chloride fundamental: 2224–1905 cm^{-1}

Line pair no.	*Wavenumber* (vac.) (cm^{-1}) $D^{35}Cl$	$D^{37}Cl$	*Line pair no.*	*Wavenumber* (vac.) (cm^{-1}) $D^{35}Cl$	$D^{37}Cl$
1	2224·04	2220·70	16	2080·28	2077·31
2	2216·96	2213·64	17	2069·27	2066·34
3	2209·62	2206·31	18	2058·05	2055·15
4	2202·00	2198·71	19	2046·61	2043·75
5	2194·13	2190·86	20	2034·96	2032·13
6	2186·00	2182·74	21	2023·10	2020·31
7	2177·61	2174·37	22	2011·04	2008·28
8	2168·96	2165·75	23	1998·78	1996·06
9	2160·07	2156·88	24	1986·32	1983·64
10	2150·93	2147·76	25	1973·66	1971·02
11	2141·54	2138·40	26	1960·82	1958·22
12	2131·91	2128·80	27	1947·78	1945·22
13	2122·05	2118·96	28	1934·57	1932·05
14	2111·95	2108·89	29	1921·17	1918·69
15	2101·62	2098·59	30	1907·59	1905·16

Data from Mould, Price and Wilkinson[28] and Plyler[38]. Cell length, 10 cm, p = 250 mm, t = 25°C, approximate spectral slit width, 0·6–1·0 cm^{-1}.


1900
1800
1740
D Br
ABSORPTION
WAVENUMBER
2
3
4
5
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7
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9
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11
12
13
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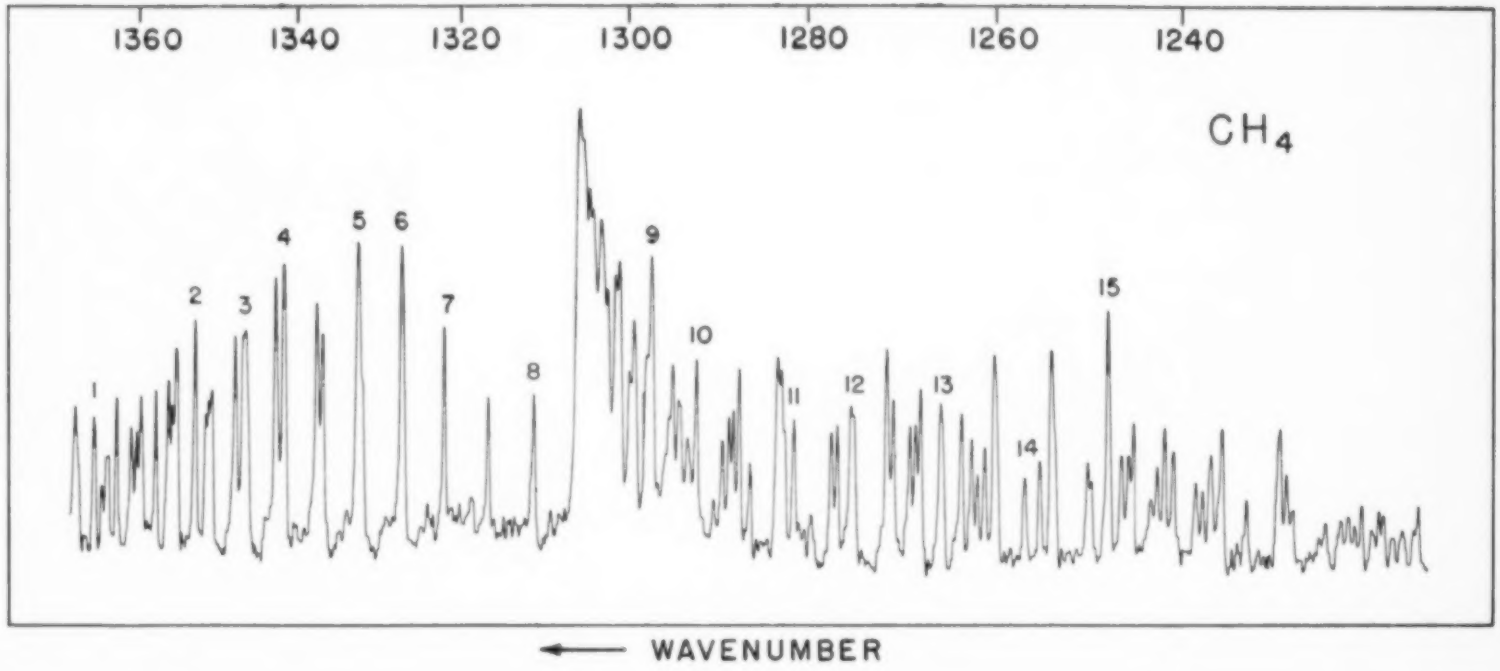
Table 13. Deuterium bromide fundamental: 1935–1727 cm^{-1}

Line pair no.	*Wavenumber* (vac.) (cm^{-1}) $D^{79}Br$	$D^{81}Br$	*av.*	*Line pair no.*	*Wavenumber* (vac.) (cm^{-1}) $D^{79}Br$	$D^{81}Br$	*av.*
1	1934·54	1933·93	1934·23	14	1831·59	1831·05	1831·32
2	1928·38	1927·79	1928·09	15	1822·93	1822·40	1822·67
3	1922·04	1921·44	1921·74	16	1814·10	1813·57	1813·83
4	1915·49	1914·90	1915·20	17	1805·12	1804·60	1804·86
5	1908·77	1908·17	1908·47	18	1795·97	1795·46	1795·72
6	1901·86	1901·27	1901·57	19	1786·67	1786·16	1786·42
7	1894·76	1894·17	1894·47	20	1777·22	1776·72	1776·97
8	1887·48	1886·90	1887·19	21	1767·61	1767·11	1767·36
9	1880·02	1879·45	1879·74	22	1757·86	1757·37	1757·62
10	1872·38	1871·81	1872·10	23	1747·96	1747·47	1747·72
11	1864·57	1864·01	1864·29	24	1737·92	1737·43	1737·68
12	1856·58	1856·02	1856·30	25	1727·74	1727·25	1727·50
13	1848·42	1847·87	1848·15				

Data from Mould, Price and Wilkinson[35] and Plyler[36]. Cell length, 10 cm, p = 60 mm, t = 25°C, approximate spectral slit width, 0·5–0·65 cm^{-1}.


1360
1340
1320
1300
1280
1260
1240
CH_4
ABSORPTION
WAVENUMBER
1
2
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15

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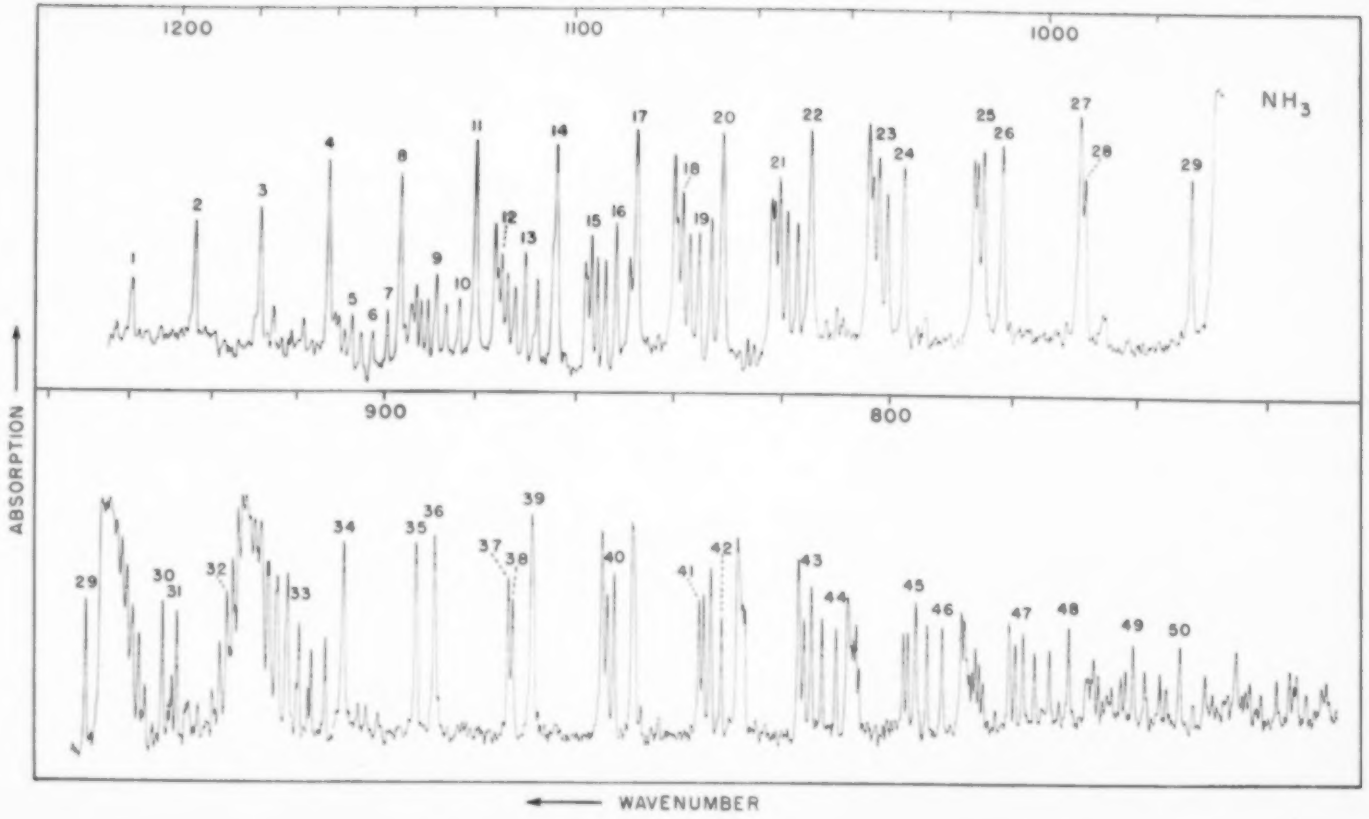
Table 14. Methane fundamental: 1366–1248 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	1366·04	9	1297·63*
2	1353·06	10	1292·61
3	1346·70*	11	1281·59
4	1341·79*	12	1275·20*
5	1332·41*	13	1265·52*
6	1327·20	14	1256·60
7	1322·09	15	1247·81
8	1311·42*		

Data from Plyler, Danti, Blaine and Tidwell[83] only. No measurements of comparable precision are available for comparison. These lines are resolution-sensitive, particularly those starred. Except for the latter, an absolute accuracy of ±0·03 is provisionally assigned. For values more suited to calibration of spectrometers with spectral slit widths of 1 cm^{-1} or larger, see Part II of these tables. Cell length, 10 cm, p = 60 mm, t = 25°C, approximate spectral slit width, 0·34 cm^{-1}.


1200
1100
1000
900
800
NH3
ABSORPTION
WAVENUMBER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
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46
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48
49
50

Table 15. Ammonia fundamental: 1213–753 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	1212·68*	19	1070·59	37	872·58
2	1195·00	20	1065·57	38	871·74
3	1177·09	21	1053·14	39	867·81*
4	1158·95	22	1046·41	40	851·35
5	1152·86*	23	1032·13	41	834·84
6	1147·53*	24	1027·04	42	830·68
7	1143·90	25	1011·21	43	814·24
8	1140·64	26	1007·55	44	809·72
9	1131·86	27	992·60*	45	796·15
10	1126·03	28	991·70*	46	791·74
11	1122·14	29	971·91	47	778·29
12	1116·03	30	951·80	48	770·92
13	1110·68	31	948·25	49	760·70
14	1103·44	32	935·90	50	753·61
15	1095·15*	33	918·62		
16	1089·39	34	908·18		
17	1084·61	35	892·04*		
18	1074·16	36	888·00		

Data from Plyler, Danti, Blaine and Tidwell[32], Mould, Price and Wilkinson[20] and Garing[29]. Agreement among these three independent sets of data indicates that the absolute accuracy of most of the lines is about $\pm 0{\cdot}03$ cm^{-1} except for the starred lines, which are resolution-sensitive. Mould, Price and Wilkinson give wavenumbers for many additional lines suitable for calibration. Cell length, 10 cm, p = 50 mm, t = 25°C, approximate spectral slit width, 0·5 cm^{-1}.

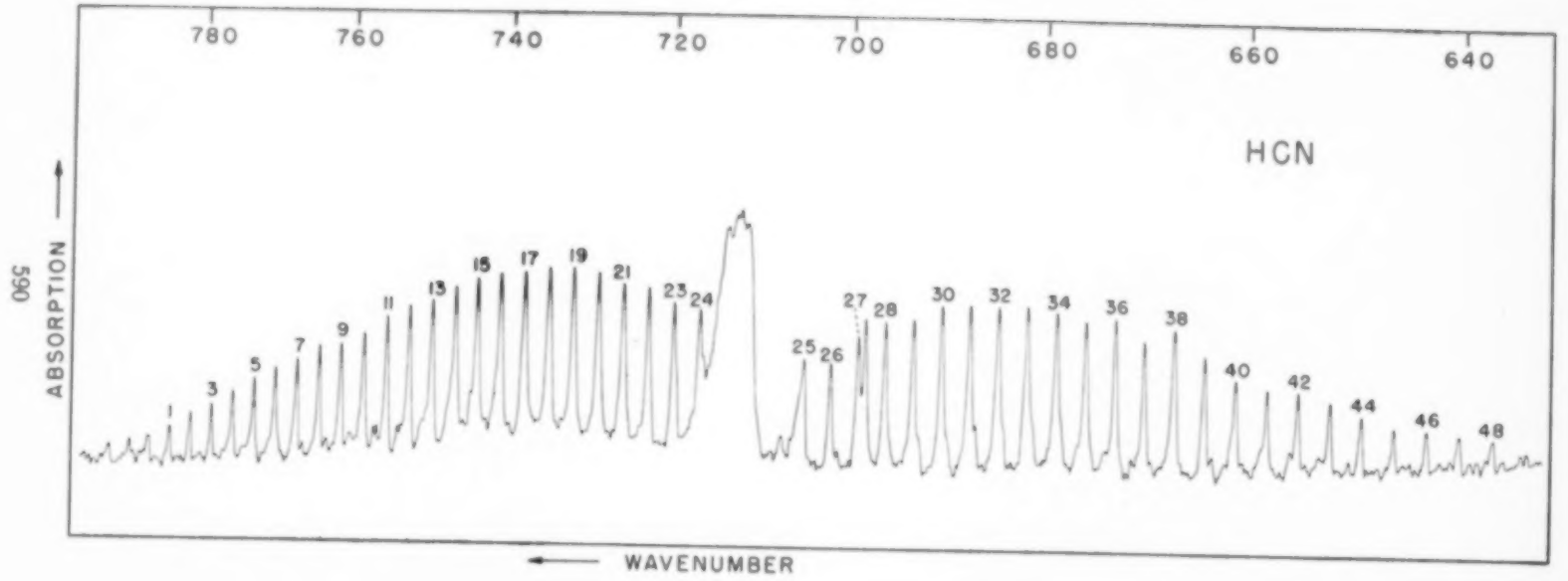
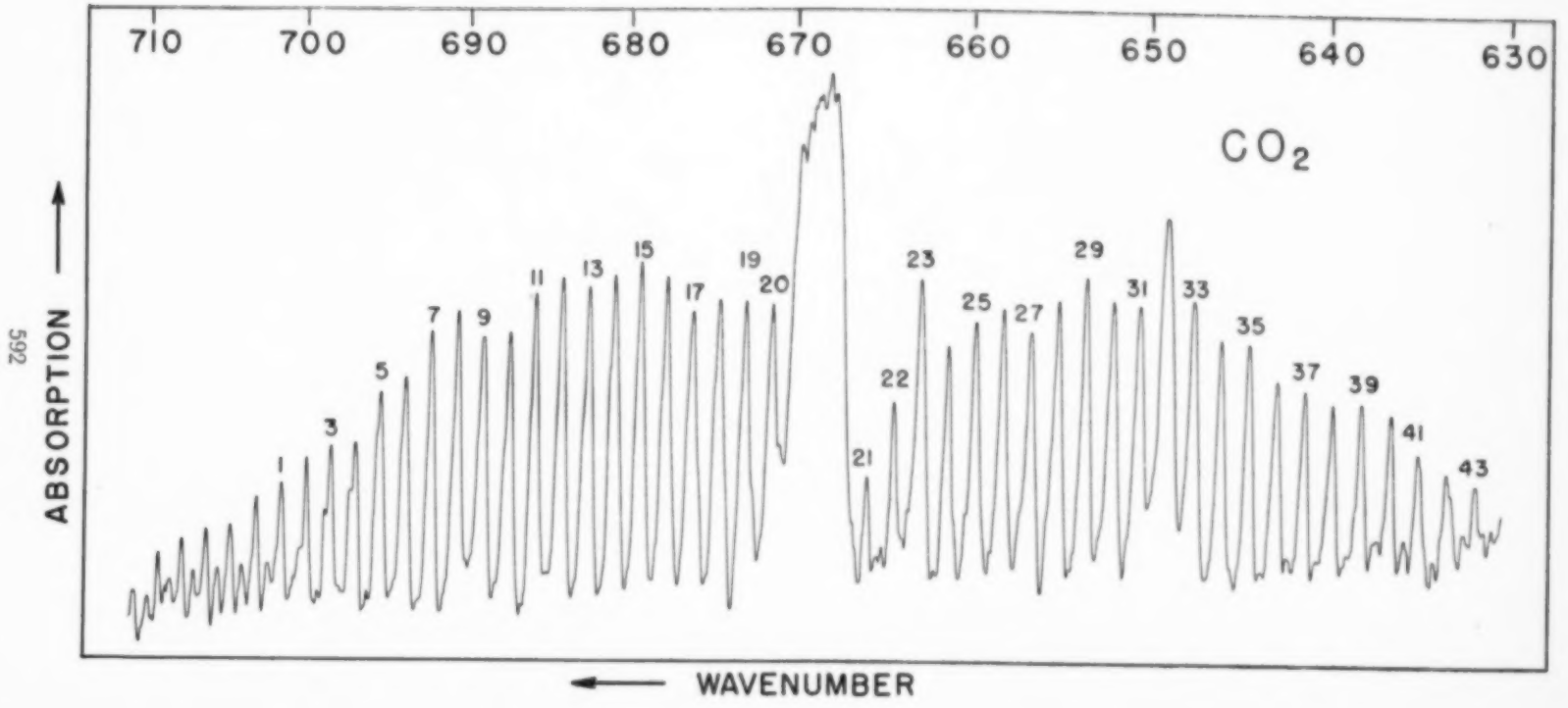

780
760
740
720
700
680
660
640
HCN
590
ABSORPTION
3
5
7
9
11
13
15
17
19
21
23
24
25
26
27
28
30
32
34
36
38
40
42
44
46
48
WAVENUMBER

Table 16. Hydrogen cyanide fundamental: 786–638 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	785·57	17	738·57	33	682·40
2	782·65	18	735·61	34	679·45
3	779·72	19	732·66	35	676·49
4	776·79	20	729·72	36	673·54
5	773·87	21	726·76	37	670·60
6	770·94	22	723·80	38	667·64
7	768·00	23	720·85	39	664·68
8	765·06	24	717·90*	40	661·73
9	762·14	25	706·08*	41	658·77
10	759·19	26	703·12	42	655·82
11	756·26	27	700·16*	43	652·88
12	753·31	28	697·19	44	649·91
13	750·37	29	694·24	45	646·97
14	747·40	30	691·29	46	644·03
15	744·45	31	688·34	47	641·07
16	741·51	32	685·36	48	638·13

Data from Rao, Brim and Hoffman[88]. The measured values of Rao, Brim and Hoffman check those calculated by Rank *et al.*[87] with the help of the combination principle to better than 0·01 cm^{-1} for most lines of low **J**-value. Hence the absolute accuracy of most of the numbers in *Table 16* is ±0·01 cm^{-1}. Cell length, 10 cm, p = 30 mm, t = 25°C, approximate spectral slit width, 0·4 cm^{-1}.


710
700
690
680
670
660
650
640
630
CO_2
ABSORPTION
WAVENUMBER
1
3
5
7
9
11
13
15
17
19
20
21
22
23
25
27
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31
33
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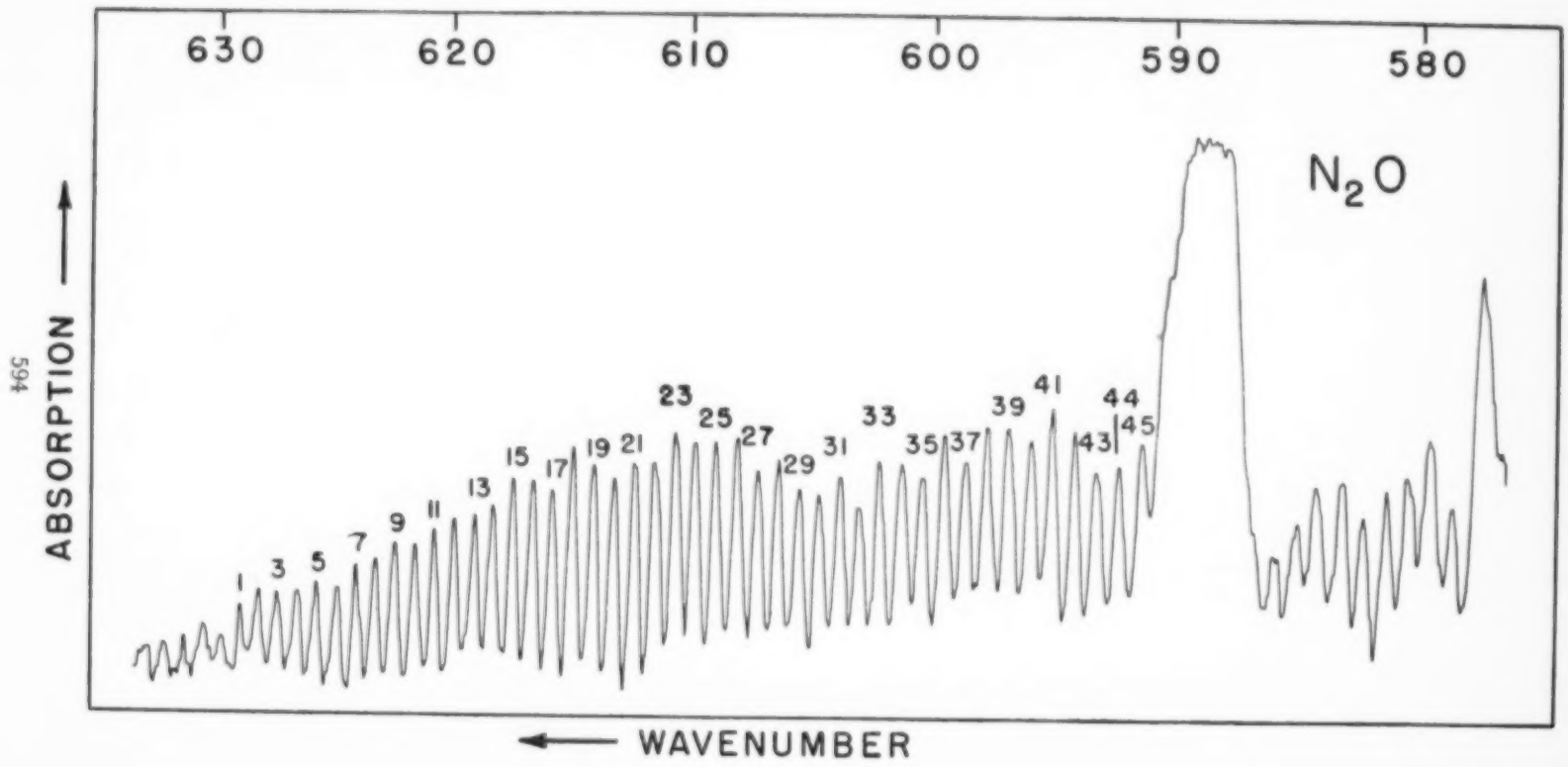
43

Table 17. Carbon dioxide fundamental: 702–629 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	701·69	16	677·60	31	650·40
2	700·07	17	676·04	32	648·90
3	698·44	18	674·45	33	647·39
4	696·82	19	672·88	34	645·90
5	695·19	20	671·34	35	644·37
6	693·59	21	665·83	36	642·86
7	691·98	22	664·28	37	641·37
8	690·37	23	662·71	38	639·83
9	688·78	24	661·17	39	638·34
10	687·16	25	659·60*	40	636·87
11	685·55	26	658·07	41	635·38
12	683·96	27	656·53	42	633·88
13	682·37	28	655·00	43	632·42
14	680·78	29	653·48	44	630·93
15	679·20	30	651·94	45	629·46

Data from Rossmann, Rao and Nielsen[39] and Plyler, Danti, Blaine and Tidwell[33]. Agreement between these two investigations implies a precision of better than ±0·02 cm^{-1} and an absolute accuracy of ±0·03 cm^{-1}. Starred line 25 is resolution-sensitive. Cell length, 10 cm, p = 70 mm, t = 25°C, approximate spectral slit width, 0·4 cm^{-1}.


630
620
610
600
590
580
N_2O
ABSORPTION
WAVENUMBER
1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
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37
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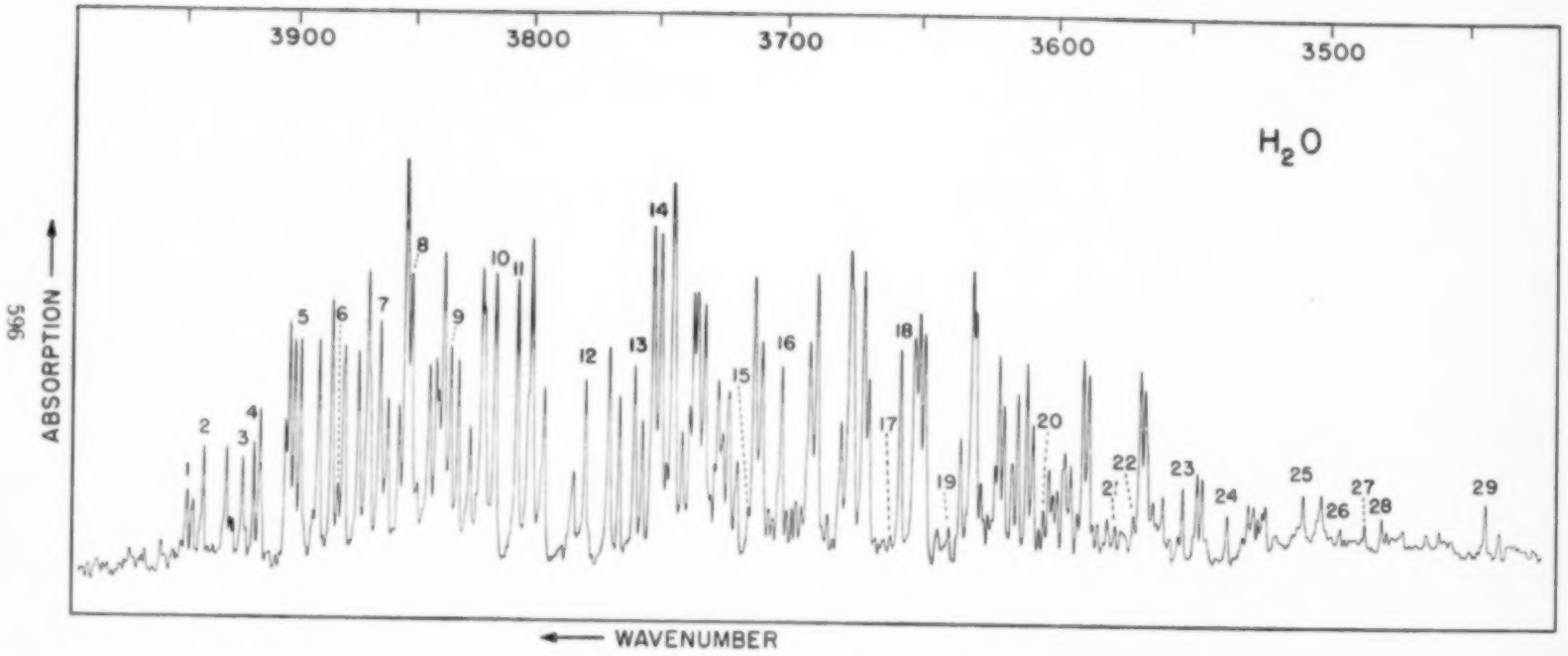
Table 18. Nitrous oxide fundamental: 630–592 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	629·29	16	616·60	31	603·91
2	628·46	17	615·74	32	603·07
3	627·61	18	614·90	33	602·23
4	626·77	19	614·06	34	601·39
5	625·93	20	613·20	35	600·54
6	625·07	21	612·35	36	599·71
7	624·22	22	611·50	37	598·87
8	623·35	23	610·65	38	598·04
9	622·53	24	609·81	39	597·22
10	621·68	25	608·98	40	596·35
11	620·84	26	608·13	41	595·52
12	619·99	27	607·29	42	594·67
13	619·14	28	606·46	43	593·82
14	618·29	29	605·61	44	592·97
15	617·44	30	604·76	45	592·13

Data from Lakshmi, Rao and Nielsen[20]. Mould, Price and Wilkinson[35] have found that the upper lines of the band tie in with those of *Table 17*, and Tidwell, Plyler and Benedict[38] have shown from the combination principle that several lines in the centre of the band are accurate to about $\pm 0{\cdot}01$ cm^{-1}. A tentative absolute accuracy of $\pm 0{\cdot}02$ cm^{-1} is estimated. Cell length, 10 cm, $p = 300$ mm, $t = 25°C$, approximate spectral slit width, 0·35 cm^{-1}.


3900
3800
3700
3600
3500
H_2O
ABSORPTION
WAVENUMBER
1
2
3
4
5
6
7
8
9
10
11
12
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1
1960

Table 19. Water vapour fundamentals: 3950–3447 cm^{-1}

(Virtually all lines should be starred as resolution-sensitive and not accurate to better than 0·1 cm^{-1})

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	3950·00	16	3701·90
2	3942·86	17	3659·94
3	3925·16	18	3656·30
4	3920·10	19	3638·15
5	3899·45	20	3603·08
6	3883·26	21	3577·06
7	3865·15	22	3570·54
8	3852·10	23	3552·35
9	3835·06	24	3536·44
10	3816·10	25	3509·49
11	3807·05	26	3496·63
12	3779·40	27	3488·11
13	3759·85	28	3482·28
14	3752·20	29	3447·20
15	3714·81		

Data from Plyler and Tidwell[22]. Path length through instrument open to the atmosphere, 320 cm, $t = 25°C$, approximate spectral slit width, 0·9 cm^{-1}. These lines are strongly pressure-sensitive and resolution-sensitive. They are not recommended for calibration purposes requiring an accuracy better than $\pm 0{\cdot}1$ cm^{-1}.

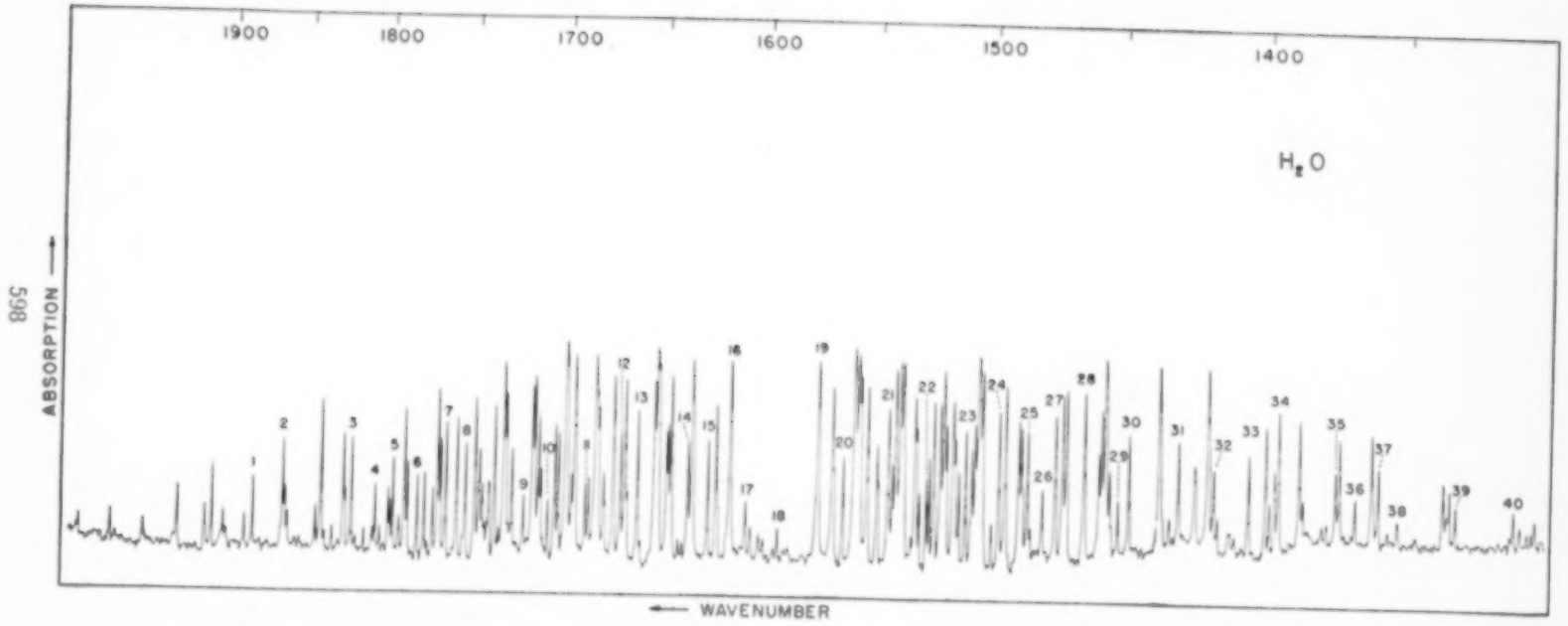

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Table 20. Water vapour fundamental: 1890–1317 cm^{-1}

Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber* (vac.) (cm^{-1})
1	1889·59	17	1609·45	33	1404·99
2	1869·36*	18	1594·51	34	1394·46*
3	1825·24	19	1576·18	35	1375·08*
4	1810·63	20	1564·87	36	1368·62
5	1799·60	21	1545·16*	37	1361·08
6	1784·95	22	1528·54*	38	1354·83
7	1768·17	23	1512·29	39	1336·62
8	1756·82	24	1498·86	40	1318·90
9	1723·48	25	1487·29		
10	1710·22	26	1481·25		
11	1690·15	27	1476·14		
12	1671·50*	28	1464·92		
13	1662·78	29	1452·06		
14	1637·53	30	1447·96		
15	1627·82	31	1429·96		
16	1616·71	32	1417·44*		

Data from Plyler, Danti, Blaine and Tidwell[53] and Rao, Ryan and Nielsen[39]. Path length through instrument open to the atmosphere, 320 cm, $t = 25°C$, approximate spectral slit width, 0·5 cm^{-1}. These lines are strongly pressure-sensitive and resolution-sensitive, particularly those starred. They are not recommended for calibration purposes requiring an accuracy better than $\pm 0{\cdot}1$ cm^{-1}.

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PART II

WAVENUMBERS FOR THE CALIBRATION OF PRISM AND SMALL GRATING SPECTROMETERS (RESOLUTION 0·5–10 cm^{-1}) IN THE RANGE 3950–600 cm^{-1}

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II. WAVENUMBERS FOR THE CALIBRATION OF PRISM AND SMALL GRATING SPECTROMETERS (RESOLUTION 0·5–10 cm^{-1}) IN THE RANGE 3950–600 cm^{-1}

INTRODUCTION

Many of the current applications of infra-red spectroscopy to the elucidation of structural and analytical problems of chemistry involve the measurement of the spectra of materials in condensed phases. Such spectra do not exhibit the rotation–vibration fine structure shown by many molecules in the vapour phase. Fine structure bands, with half-widths of less than 2 cm^{-1} occur occasionally in association with the lattice vibrations of crystals, but most solids and liquids exhibit structure-less vibration absorption bands, the half-widths of which are seldom less than 2 cm^{-1} and usually greater than 5 cm^{-1}.

In the investigation of such spectra it has been customary to employ prism spectrometers. The resolution achieved by these instruments depends on the optical design and the nature of the prism material; it may also vary widely for the same spectrometer in different regions of the spectrum. The more elaborate prism spectrometers in current use may achieve nominal spectral slit widths in the range 1–2 cm^{-1}, but they are severely energy-limited. To obtain an acceptable signal-to-noise ratio it is usually necessary to use wide slits, or else high amplifier gain combined with a narrow electrical band-pass frequency. Widening the slits leads directly to a reduction in the resolution, while decreasing the band-pass frequency causes a virtual loss of resolution and increases the instrumental distortion of the band shape. These latter effects may be partly offset by a reduction in the scanning speed, but there are practical limits to the use of such corrective measures. In view of these considerations, most prism spectrometers are operated at nominal spectral slit widths exceeding 2 cm^{-1}, and commonly in the range 2–10 cm^{-1}.

Because of their greater overall efficiency, increasing use is now being made of small grating spectrometers in the measurement of condensed phase spectra. When so used the most efficient operating conditions of the spectrometer will differ from those applicable to the measurement of vapour phase vibration–rotation spectra. The intrinsic broadness of the bands permits the use of wider slits without loss of structural detail or significant distortion of the spectrum. Optimal spectral slit widths in the range 1–2 cm^{-1} can often be used, permitting higher signal-to-noise ratios and faster scanning speeds.

The wavenumber calibration tables in Part II have been prepared by the

Commission to meet the requirements of grating spectrometers operating under these conditions, as well as prism spectrometers operating under a wide range of conditions encountered in applied chemical spectroscopy.

ARRANGEMENT OF THE TABLES

Charts 1–34

Charts 1–34 demonstrate vapour phase spectra for the wavenumber range 3950–590 cm^{-1}, each chart covers a span of 100 cm^{-1}. The same calibrant gases are used as for the Part I tables, supplemented by deuterium cyanide. The spectral ranges covered by each gas are listed on the following page. Whereas the lines listed in the corresponding tables of Part I have been chosen solely for their suitability as accurate wavenumber standards, additional factors have also been taken into consideration in the choice of the calibration lines in Part II.

Because of the intrinsic broadness of the bands in condensed-phase spectra, there is usually less need for extreme precision in the evaluation of wavenumber, and for most purposes an absolute accuracy between 0·1 and 0·5 cm^{-1} will suffice. The positions of the calibration lines listed in Part II have therefore been rounded to the nearest $0{\cdot}05_5$ cm^{-1}. This wider tolerance permits the inclusion of lines that do not meet the more critical specifications of the Part I data. In particular, it diminishes the significance of small line displacements resulting from pressure broadening, and from resolution effects on partial line overlap. Higher pressures may be used, so that bands can be followed out to higher **J**-numbers, and this assists materially in eliminating gaps between the ranges of different calibrant gases. Greater tolerance of small resolution-sensitive overlap effects allows the inclusion of additional lines and a more even distribution of calibration points across the spectrum. Uncertainties which may be introduced by these pressure- and resolution-sensitive displacements are compensated by a reduction in interpolation errors when instrumental scale readings are converted to wavenumber units by the methods outlined on p. 20 of Part I.

In several of the charts the wavenumber positions of closely lying doublet and triplet line groups have been recorded. These are indicated as "resolution tests" in the tables accompanying *Charts 1–34*, and are intended for the evaluation and control of spectrometer performance. Lines that appear in the tables of both Parts I and II are identified by the symbol †.

Particular features of the individual spectra which affect their use for calibration purposes are dealt with in footnotes to the individual tables, but there are a few additional matters calling for more general comment.

(*a*) *Ammonia* (*3540–3394 cm*$^{-1}$)—In the Part I calibration tables a gap extends from 3579 to 3386 cm^{-1} for which the Commission has been unable to locate any lines of acceptable accuracy. The ν_1 fundamental band in the spectrum of ammonia occupies this region, but the lines are highly resolution-sensitive and are judged unsuitable for high precision calibration on this account. Blends of some of these lines are included in *Charts 5* and *6* in order to provide some calibration points in this region, which is particularly important in the investigation of hydrogen bonding phenomena. For these blended lines an absolute accuracy of only $\pm 0{\cdot}2$ cm^{-1} is claimed, and it is

Summary of data for Charts 1–39
(All vapour phase spectra are measured at 10 cm path length)

Substance	*Region* (cm^{-1})	*Pressure* (mm)	*Chart no.*
Water vapour	3943–3744	sat.	1–3
Carbon dioxide	3737–3683	200	3–4
,,	3681–3591	400	4
,,	3608–3569	200	5
Ammonia	3540–3491	300	5
,,	3509–3394	75	6
Hydrogen cyanide	3399–3381	450	7
,,	3378–3245	20	7–8
,,	3231–3207	450	8
Methane	3183–3158	300	9
,,	3149–2958	60	9–11
Hydrogen chloride	3045–2624	120	10–14
Hydrogen bromide	2710–2393	140	14–17
Carbon dioxide	2386–2298	20	17
,,	2311–2292	50	18
,,	2282–2236	250	18
Carbon monoxide	2233–2055	150	18–20
Deuterium chloride	2047–1894	250	19–21
Water vapour	1943–1374	sat.	21–27
Deuterium bromide	1909–1727	60	22–23
Ammonia	1613–1580	75	24–25
Methane	1368–1266	60	27–28
,,	1260–1212	250	28
Ammonia	1213– 972	50	28–31
,,	967– 962	15	31
,,	960– 934	50	31
,,	927– 924	15	31
,,	921– 771	50	31–33
,,	761– 745	75	33
Hydrogen cyanide	786– 635	30	33–34
Acetylene	720– 694	15	33
Carbon dioxide	702– 632	70	34
Nitrous oxide	630– 593	300	34
Deuterium cyanide	630– 591	60	34
Indene	3929– 693	*	35–37
Polystyrene	3082– 699	†	38–39

* Liquid films of thickness 200 μ and 30 μ.
† Solid films of thickness 70 μ and 7 μ.

essential that in using them the resolution of the calibration spectrum be matched as closely as possible.

(*b*) *Water vapour (3950–3750 cm^{-1}; 1940–1370 cm^{-1})*—The water vapour lines selected for inclusion in Part I are based on measurements at long path lengths (2–7 m), and some of them appear weak when observed at a path length of 10 cm of saturated water vapour at room temperature. It was considered desirable that all vapour spectra used in Part II should be based on a 10 cm path length, as the use of longer path lengths is inconvenient, particularly when working with flushed or evacuated spectrometers or when calibrating by the superposition method (Part I, p. 556). In the Part II water vapour spectra stronger lines have in some instances been selected in place of the Part I calibration lines on this account. It is of practical interest to note

that the water lines are best observed with a cell containing a small amount of liquid water and thin silver chloride windows. The windows should be slightly deformed to eliminate interference patterns. The line intensities can be augmented by aspirating air or nitrogen through a water wash-bottle containing a sintered glass bubbler, and then through the cell.

On *Charts 24* and *25* the use of six lines from the spectrum of ammonia is recommended to supplement the water vapour spectrum in the region of the weak *Q*-branch absorption.

(*c*) *Deuterium cyanide* (*630–590 cm*$^{-1}$)—Lines from this spectrum have been added to supplement the nitrous oxide lines because the latter are too close to be resolved at spectral slit widths wider than 0·5 cm^{-1}. These data are based on the work of Checkland and Thompson (*Trans. Faraday Soc.*, **51**, 1 (1955)), and unpublished measurements of Jones.

Measurements at lower resolution; Charts 1A–34A

As the resolution of the spectrometer is diminished, the apparent half line width increases and the determination of absolute line position becomes more uncertain. It is difficult to predict the magnitude of such effects on particular groups of lines. The spectra have therefore been remeasured on a carefully calibrated grating spectrometer at a series of gradually increasing slit schedules. The lines which are least affected are distinguished by the symbol (*) in the tables accompanying *Charts 1–34*.

These lines are also indicated on *Charts 1A–34A* and they are recommended for the calibration of prism spectrometers under conditions where the resolution of *Charts 1A–34A* can be matched or exceeded. Most of these spectra were determined at nominal spectral slit widths in the range 1·5–3 cm^{-1} which should be within the capabilities of the larger prism instruments. *Charts 3A*, *4A*, *5A*, *17A*, *18A*, *33A* and *34A* were measured at nominal spectral slit widths of 1–1·5 cm^{-1}, conditions which it may be difficult to achieve with conventional prism spectrometers under routine operating conditions. The accuracy of the line positions under the conditions of *Charts 1A–34A* should not differ greatly from that reported in the tables; an increase in tolerance by a factor of two might reasonably be allowed. On the broader lines the major uncertainty will lie in the evaluation of the position of the curve maximum.

Charts 35–39; liquid and solid phase calibrant materials for small prism spectrometers

The smaller types of prism spectrometers are difficult to calibrate from vapour phase spectra because their low dispersion does not resolve a sufficient number of calibration lines, and the interpolation errors become increasingly large. This is true particularly where a sodium chloride prism is utilized above 2000 cm^{-1}.

Interpolation techniques for dealing with this situation have been proposed by McKinney and Friedel (*J. Opt. Soc. Am.*, **38**, 222 (1948)), and by Bethke (*J. Opt. Soc. Am.*, **46**, 560 (1956)). Their use, with specific applications to various categories of prism spectrometers, has been outlined by Downie, Magoon, Purcell and Crawford (*J. Opt. Soc. Am.*, **43**, 941 (1956)). Because

of limitations inherent in the optical and mechanical design of these smaller instruments, it is unlikely that spectrometers of this type will be capable of a precision better than ± 1 cm^{-1} through most regions of the spectrum, and it is more convenient, and probably no less accurate, to calibrate with carefully measured vibrational bands from the spectra of selected liquids and solids.

It is the view of the Commission that more extensive measurements of this kind are desirable to provide a wider range of liquid and solid phase spectra suitable for this purpose. In *Charts 35–39* the spectra of liquid indene and of a polystyrene film are reproduced. The provisional band positions listed in the accompanying tables are taken from the data of Jones, Jonathan, Nadeau and MacKenzie (*Spectrochim. Acta*, in press) for indene and of Plyler, Danti, Blaine and Tidwell (*J. Research Natl. Bur. Standards*, **64**, 29 (1960)), and Jones and Nadeau (unpublished) for polystyrene.

Collectively these spectra provide approximately one hundred provisional calibration points, most of which should be within the resolution capabilities of the small prism spectrometers under consideration. These data should allow calibration of such instruments with a precision of ± 1 cm^{-1} providing spectral slit widths of 10 cm^{-1} or less can be achieved.

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Preparation of gaseous samples

The majority of the gases are readily obtained from commercial sources. Deuterium chloride is conveniently prepared by the drop-wise action of deuterium oxide on phosphorus pentachloride at room temperature. Deuterium bromide is similarly obtainable from deuterium oxide and phosphorus tribromide with gentle warming. Deuterium cyanide can be prepared by the action of dideutero-sulphuric acid on potassium cyanide, or alternatively from phosphorus pentoxide, deuterium oxide and potassium cyanide as described by Richardson (*J. Phys. Chem.*, **19**, 1213 (1951)).

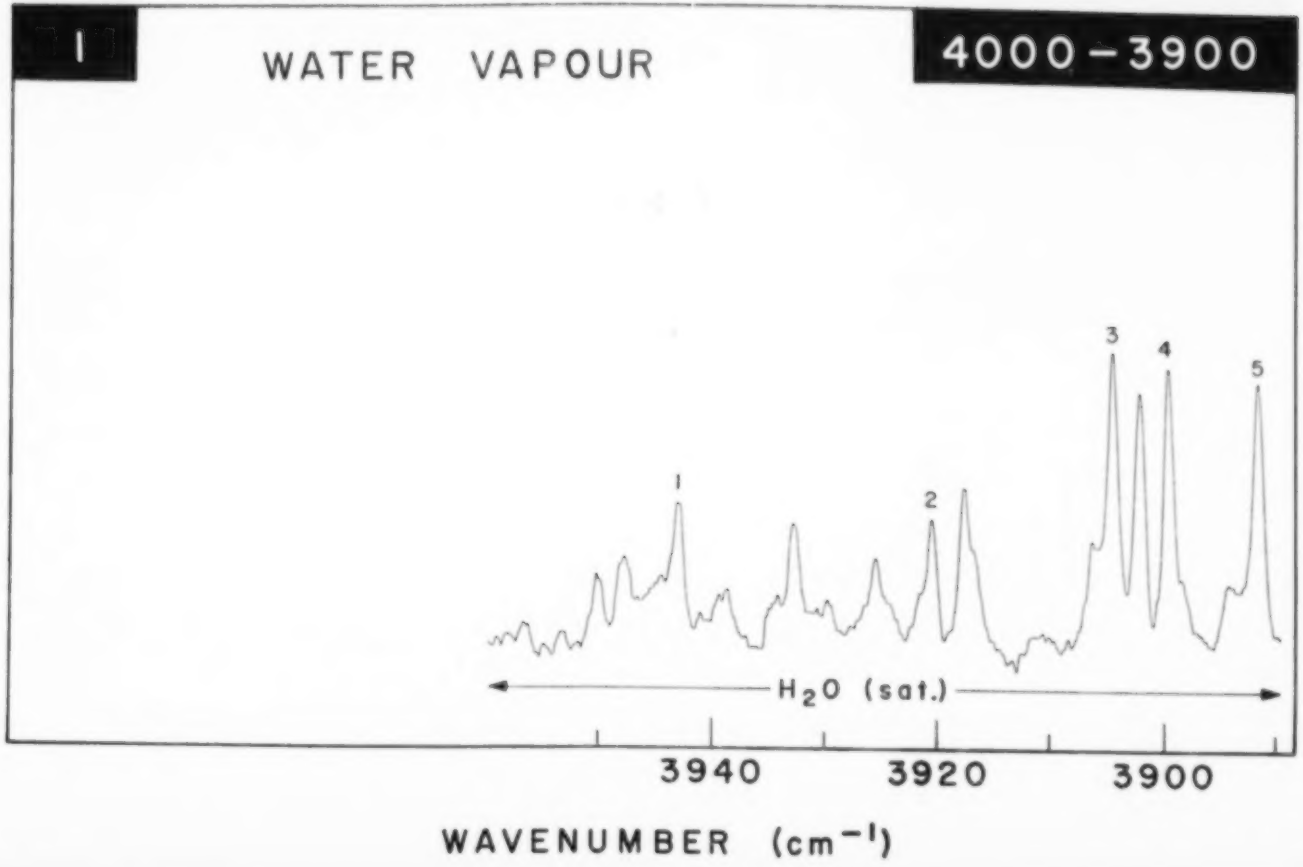
1
WATER VAPOUR
4000–3900
1
2
3
4
5
H_2O (sat.)
3940
3920
3900
WAVENUMBER (cm^{-1})

Chart 1. Water vapour (saturated): 3950–3900 cm^{-1}

Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})
1	$3942{\cdot}8_\delta$ †‡
2	3920·1†
3	$3904{\cdot}2_\delta$
4	$3899{\cdot}4_\delta$†
5	3891·3‡

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 1A*).
(a) Most of these lines are blends and will resolve under higher resolution (Part I).
(b) The estimated uncertainty does not exceed $\pm 0{\cdot}1\ cm^{-1}$.

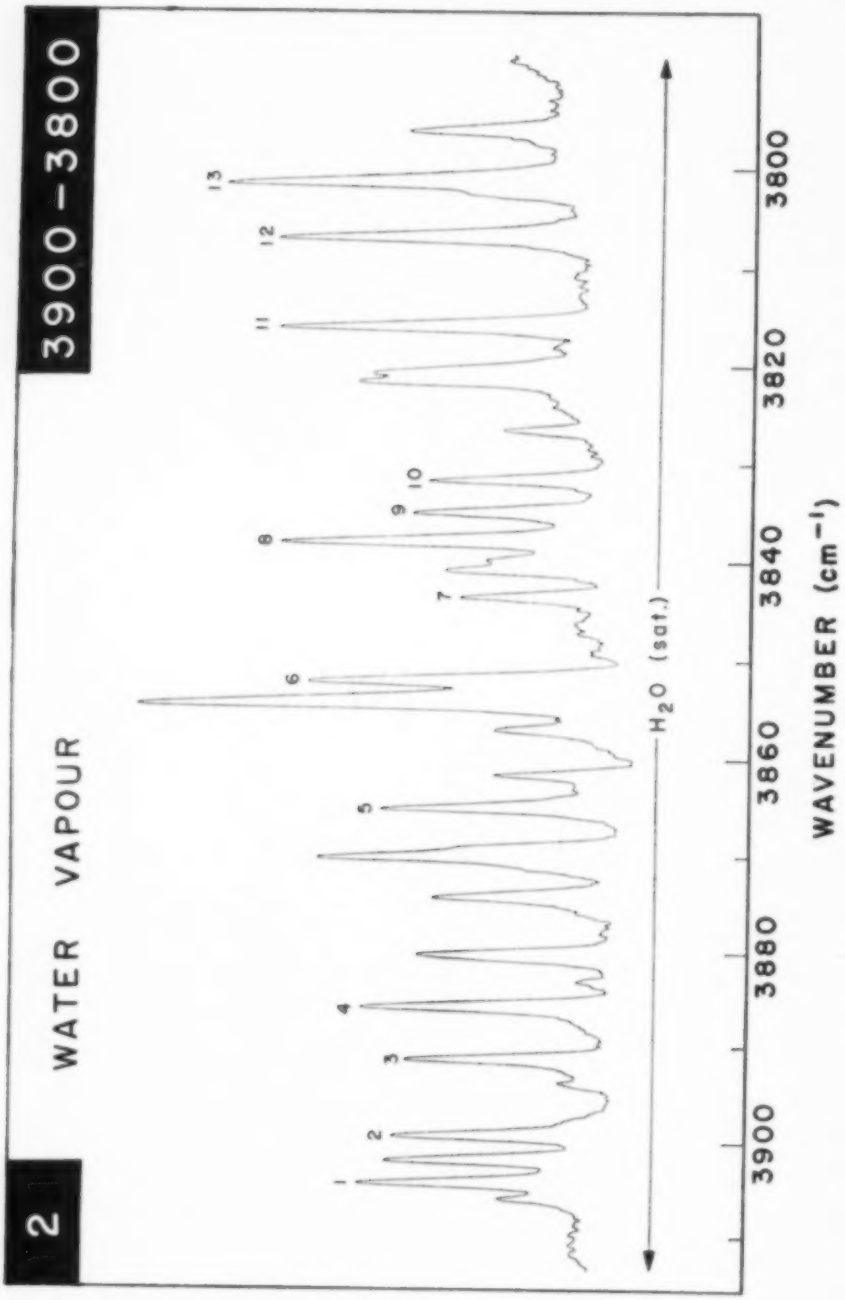
2
WATER VAPOUR
3900–3800
1
2
3
4
5
6
7
8
9
10
11
12
13
H_2O (sat.)
3900
3880
3860
3840
3820
3800
WAVENUMBER (cm^{-1})

Chart 2. Water vapour (saturated): 3900–3800 cm^{-1}

Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a,b] (vac.) (cm^{-1})
1	$3904{\cdot}2_5$	7	3843·8
2	$3899{\cdot}4_5$†	8	3837·9‡
3	3891·3‡	9	$3835{\cdot}0_5$†
4	3885·9‡	10	$3831{\cdot}7_5$‡
5	$3865{\cdot}1_5$†‡	11	3816·1†‡
6	3852·1†	12	$3807{\cdot}0_5$†‡
		13	$3801{\cdot}4_5$‡
Resolution tests:	Line no. 8–line no. 9: 2·85 cm^{-1} Line no. 9–line no. 10: 3·35 cm^{-1}		

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 2A*).
(a) Most of these lines are blends and will resolve under higher resolution (Part I).
(b) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

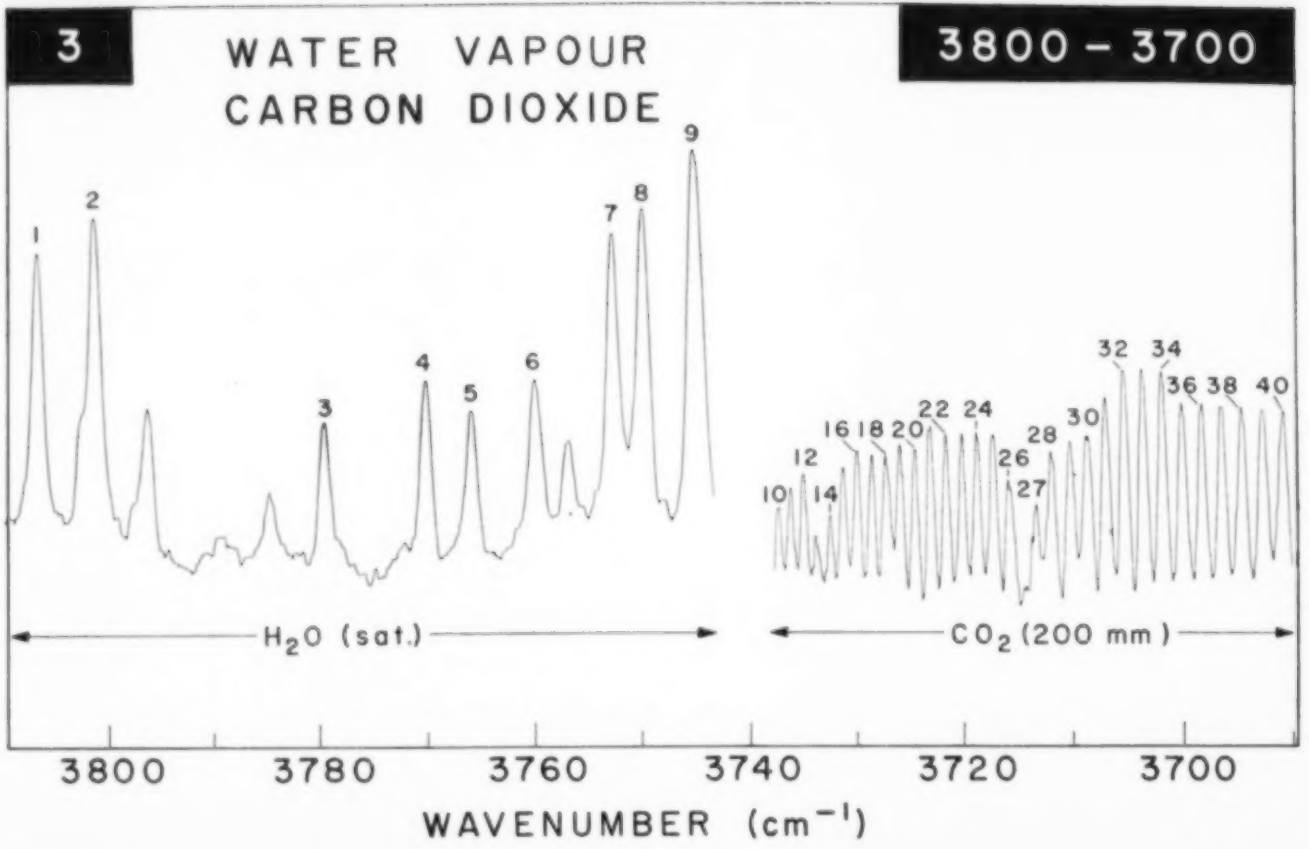
3
WATER VAPOUR
CARBON DIOXIDE
3800 - 3700
1
2
3
4
5
6
7
8
9
10
12
14
16
18
20
22
24
26
27
28
30
32
34
36
38
40
H2O (sat.)
CO2 (200 mm)
3800
3780
3760
3740
3720
3700
WAVENUMBER (cm-1)

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Chart 3. Water vapour (saturated) and carbon dioxide (200 mm): 3800–3700 cm^{-1}

Water vapour (saturated)		*Carbon dioxide* (200 mm)			
Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})
1	$3807{\cdot}0_5$†‡	10	3737·0	25	3717·1‡
2	3801·4‡	11	$3735{\cdot}8_5$	26	$3715{\cdot}5_5$
3	3779·4†	12	3734·7	27	3713·2
4	3769·8‡	13	3733·5†	28	$3711{\cdot}6_5$
5	3765·8	14	3732·2	29	3710·0
6	$3759{\cdot}8_5$†‡	15	3731·0†	30	3708·4†
7	3752·2†‡	16	$3729{\cdot}7_5$†	31	3706·7†‡
8	3749·3‡	17	3728·4†	32	3705·0†‡
9	3744·5‡	18	$3727{\cdot}0_5$‡	33	3703·3†‡
		19	3725·7†	34	$3701{\cdot}5_5$‡
		20	$3724{\cdot}3_5$†	35	3699·8†‡
		21	3722·9†‡	36	3698·0†‡
		22	3721·5‡	37	$3696{\cdot}1_5$‡
		23	3720·1†‡	38	$3694{\cdot}3_5$†‡
		24	3718·6‡	39	$3692{\cdot}4_5$†‡
				40	$3690{\cdot}5_5$‡

Resolution tests: Line no. 16–line no. 17: 1·35 cm^{-1}
Line no. 32–line no. 33: 1·7 cm^{-1}
Line no. 7–line no. 8: 2·9 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 3A*); where the dispersion is insufficient to resolve these lines, the line at 3701·9 cm^{-1} in the spectrum of water vapour may be employed as a calibration point.
(a) Most of these lines are blends and will resolve under higher resolution (Part I).
(b) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

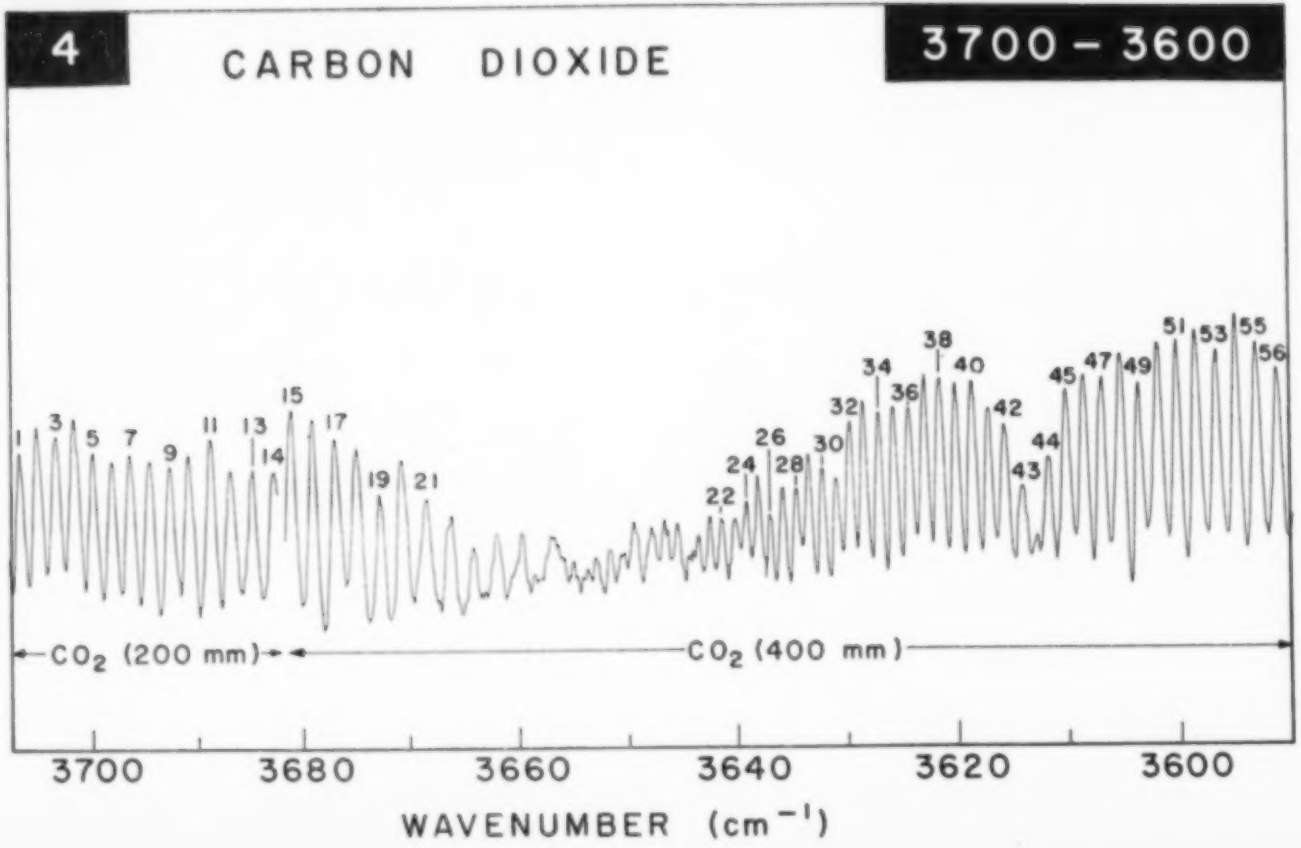
4
CARBON DIOXIDE
3700 - 3600
1 3 5 7 9 11 13 14 15 17 19 21 22 24 26 28 30 32 34 36 38 40 42 43 44 45 47 49 51 53 55 56
CO2 (200 mm)
CO2 (400 mm)
3700 3680 3660 3640 3620 3600
WAVENUMBER (cm-1)

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Chart 4. Carbon dioxide (200 mm) and (400 mm): 3700–3600 cm^{-1}

Carbon dioxide (200 mm)		*Carbon dioxide* (400 mm)			
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	3706·7†‡	15	$3680\text{·}7_5$‡	36	$3623\text{·}9_5$†‡
2	3705·0†‡	16	3678·7‡	37	3622·5†‡
3	3703·3†‡	17	$3676\text{·}6_5$	38	$3621\text{·}1_5$†‡
4	$3701\text{·}5_5$‡	18	3674·6	39	3619·6‡
5	3699·8†‡	19	3672·5	40	$3618\text{·}1_5$‡
6	3698·0†‡	20	$3670\text{·}3_5$‡	41	$3616\text{·}6_5$‡
7	$3696\text{·}1_5$‡	21	3668·2‡	42	$3615\text{·}2_5$†‡
8	$3694\text{·}3_5$†‡	22	3641·1	43	3613·6
9	$3692\text{·}4_5$	23	3640·0†	44	3611·3
10	$3690\text{·}5_5$‡	24	$3638\text{·}9_5$	45	3609·7‡
11	$3688\text{·}6_5$‡	25	3637·8	46	$3608\text{·}0_5$†‡
12	$3686\text{·}7_5$†‡	26	$3636\text{·}6_5$	47	3606·5†‡
13	$3684\text{·}7_5$‡	27	3635·5	48	3604·8†‡
14	3682·8†‡	28	3634·3	49	3603·1‡
		29	$3633\text{·}0_5$	50	3601·4†‡
		30	$3631\text{·}8_5$†	51	$3599\text{·}7_5$†‡
		31	$3630\text{·}5_5$	52	$3598\text{·}0_5$‡
		32	3629·3	53	3596·2†‡
		33	3628·0	54	3594·4†‡
		34	3626·6	55	$3592\text{·}6_5$†‡
		35	$3625\text{·}2_5$†	56	3590·8†‡

Resolution tests: Line no. 34–line no. 35: 1·35 cm^{-1}
Line no. 51–line no. 52: 1·75 cm^{-1}
Line no. 7–line no. 8: 1·80 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 4A*); where the dispersion is insufficient to resolve these lines, the lines at 3701·9 and 3656·3 cm^{-1} in the spectrum of water vapour may be employed as calibration points.
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

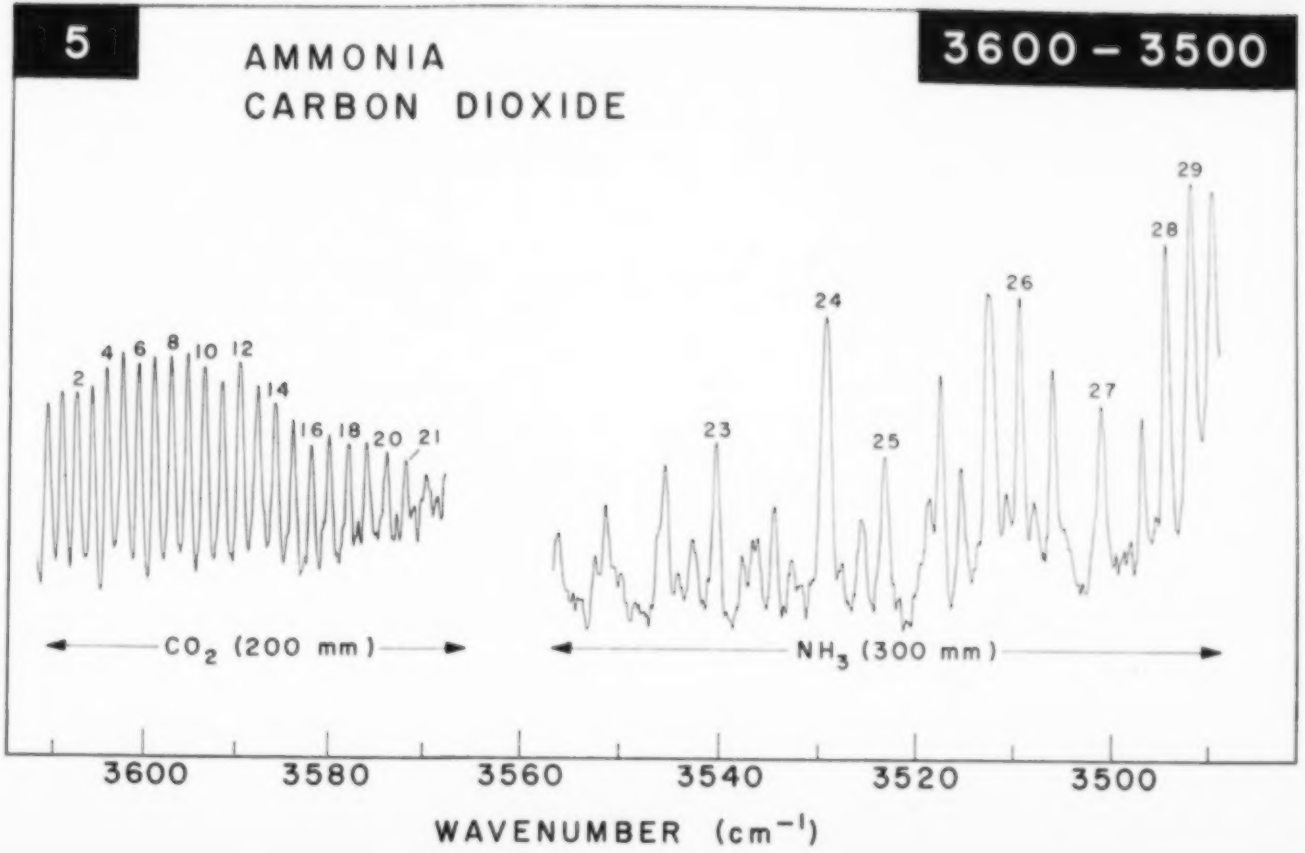
5
AMMONIA
CARBON DIOXIDE
3600 – 3500
2
4
6
8
10
12
14
16
18
20
21
23
24
25
26
27
28
29
CO2 (200 mm)
NH3 (300 mm)
3600
3580
3560
3540
3520
3500
WAVENUMBER (cm−1)

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Chart 5. Carbon dioxide (200 mm) and ammonia (300 mm): 3600–3500 cm^{-1}

Carbon dioxide (200 mm)		*Ammonia* (300 mm)			
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b c] (vac.) (cm^{-1})
1	$3608{\cdot}0_5$‡	12	$3588{\cdot}9_5$‡	23	3540·1
2	3606·5†‡	13	3587·1‡	24	3529·0‡
3	3604·8†‡	14	3585·2†‡	25	3523·1‡
4	$3603{\cdot}1_5$‡	15	$3583{\cdot}2_5$‡	26	$3508{\cdot}9_5$‡
5	3601·4†‡	16	3581·3†‡	27	3500·4‡
6	$3599{\cdot}7_5$†‡	17	$3579{\cdot}3_5$†‡	28	3493·9‡
7	3598·0‡	18	$3577{\cdot}3_5$‡	29	3491·4
8	3596·2†‡	19	3575·4		
9	3594·4†‡	20	3573·4		
10	$3592{\cdot}6_5$†‡	21	3571·3		
11	3590·8†‡	22	3569·2		

Resolution tests: Line no. 9–line no. 10: 1·75 cm^{-1}
Line no. 28–line no. 29: 2·5 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 5A*).
(a) The estimated uncertainty does not exceed $\pm 0{\cdot}1$ cm^{-1}.
(b) The estimated uncertainty is $\pm 0{\cdot}2$ cm^{-1}.
(c) These lines are all blends and should not be used for calibration if the resolution exceeds that shown in *Chart 5*.

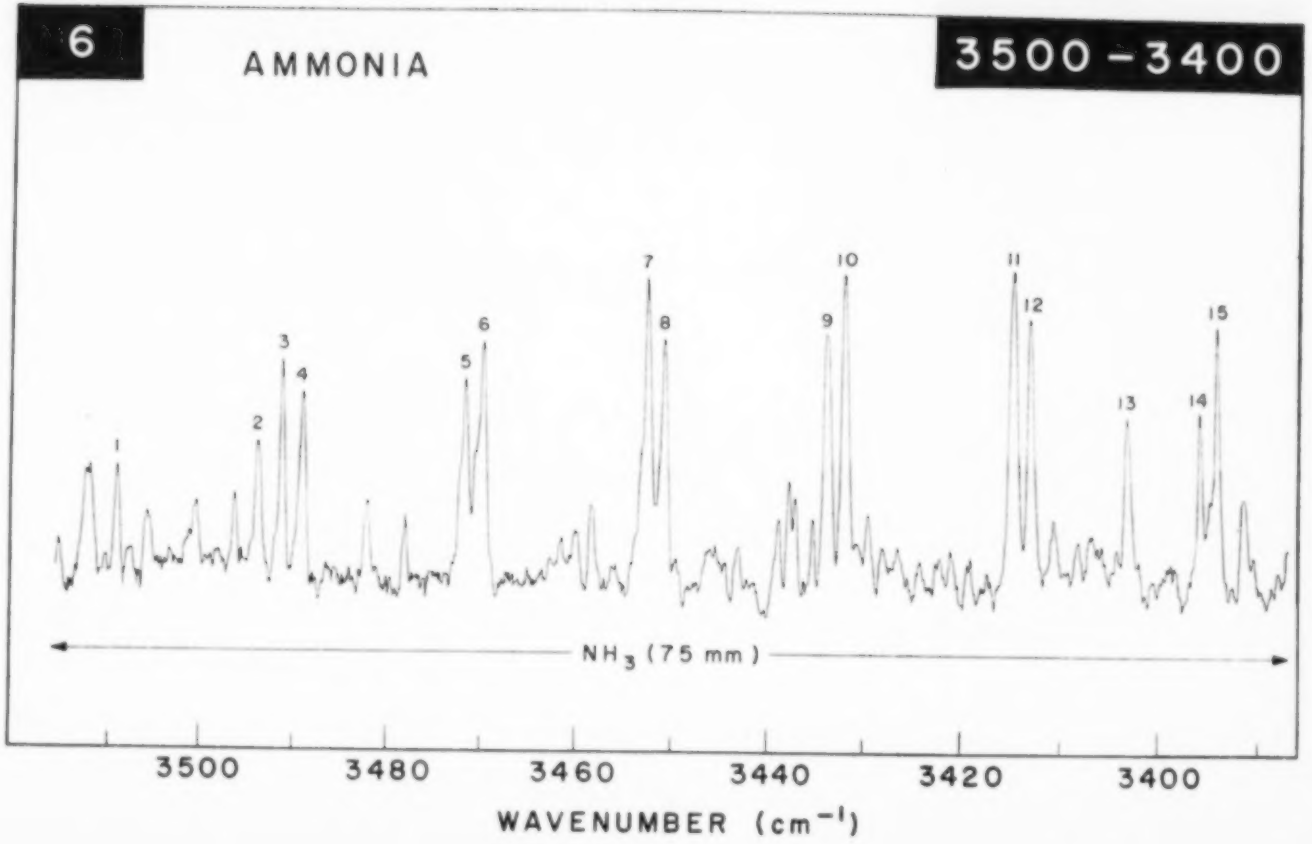
6
AMMONIA
3500 – 3400
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
NH3 (75 mm)
3500
3480
3460
3440
3420
3400
WAVENUMBER (cm⁻¹)

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Chart 6. Ammonia (75 mm): 3500–3400 cm^{-1}

Line no.	*Wavenumber*‡[a, b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*‡[a, b] (vac.) (cm^{-1})
1	3508·9[a]	9	3433·8
2	3493·9	10	3432·0
3	3491·4	11	3414·7
4	3489·3	12	3413·1
5	3471·7	13	3403·1‡
6	3469·8	14	3395·6[a]
7	3452·7	15	3393·9
8	3450·9		

Resolution tests: Line no. 7–line no. 8: 1·8 cm^{-1}

‡ Under lower resolution (*Chart 6A*) only line no. 13 remains as an acceptable calibration point. The blended lines no. 5/6, 7/8, 9/10, 11/12, and 14/15 have peaks at 3470·4 cm^{-1}, 3452·1 cm^{-1}, 3432·6 cm^{-1}, 3414·1 cm^{-1}, and 3394·5 cm^{-1} under the conditions shown in *Chart 6A*. These values can be used for calibration purposes to ± 0·5 cm^{-1}.

(a) These lines are all blends and should not be used for calibration if the resolution exceeds that shown in *Chart 6*.

(b) The estimated uncertainty is ± 0·2 cm^{-1}.

7
HYDROGEN CYANIDE
3400–3300
HCN (450 mm)
HCN (20 mm)
WAVENUMBER (cm⁻¹)
3400
3380
3360
3340
3320
3300
1
3
5
7
9
10
12
14
16
18
20
22
24
26
28
30
32
33
34
35
36
37
38
39
40
41

Chart 7. Hydrogen cyanide (450 mm) and (20 mm): 3400–3300 cm^{-1}

Hydrogen cyanide (450 mm)		*Hydrogen cyanide* (20 mm)			
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	$3399{\cdot}1_5$	10	$3378{\cdot}4_5$†	26	$3337{\cdot}1_5$†‡
2	$3396{\cdot}9_5$	11	3376·0†	27	$3334{\cdot}3_5$†‡
3	3394·7	12	3373·6†	28	3331·6†‡
4	$3392{\cdot}4_5$	13	3371·1†	29	3328·8†‡
5	3390·2	14	$3368{\cdot}6_5$†	30	$3325{\cdot}9_5$†‡
6	3387·9	15	$3366{\cdot}1_5$†	31	3323·1†‡
7	$3385{\cdot}5_5$†	16	3363·6†	32	3320·2†‡
8	3383·2†	17	$3361{\cdot}0_5$†	33	3317·3‡
9	$3380{\cdot}8_5$†	18	3358·5†	34	3314·4
		19	3355·9†	35	3308·5†
		20	3353·3†	36	$3305{\cdot}5_5$†
		21	$3350{\cdot}6_5$†‡	37	$3302{\cdot}5_5$†
		22	3348·0†‡	38	3299·5†‡
		23	3345·3†‡	39	3296·5†‡
		24	3342·6†‡	40	3293·4†‡
		25	3339·9†‡	41	$3290{\cdot}3_5$†‡

Resolution tests: Line no. 7–line no. 8: 2·35 cm^{-1}
Line no. 25–line no. 26: 2·75 cm^{-1}
Line no. 39–line no. 40: 3·1 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 7A*); the unresolved ammonia line complex at 3394·5 ±0·5 cm^{-1} may also be employed (*Chart 6A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

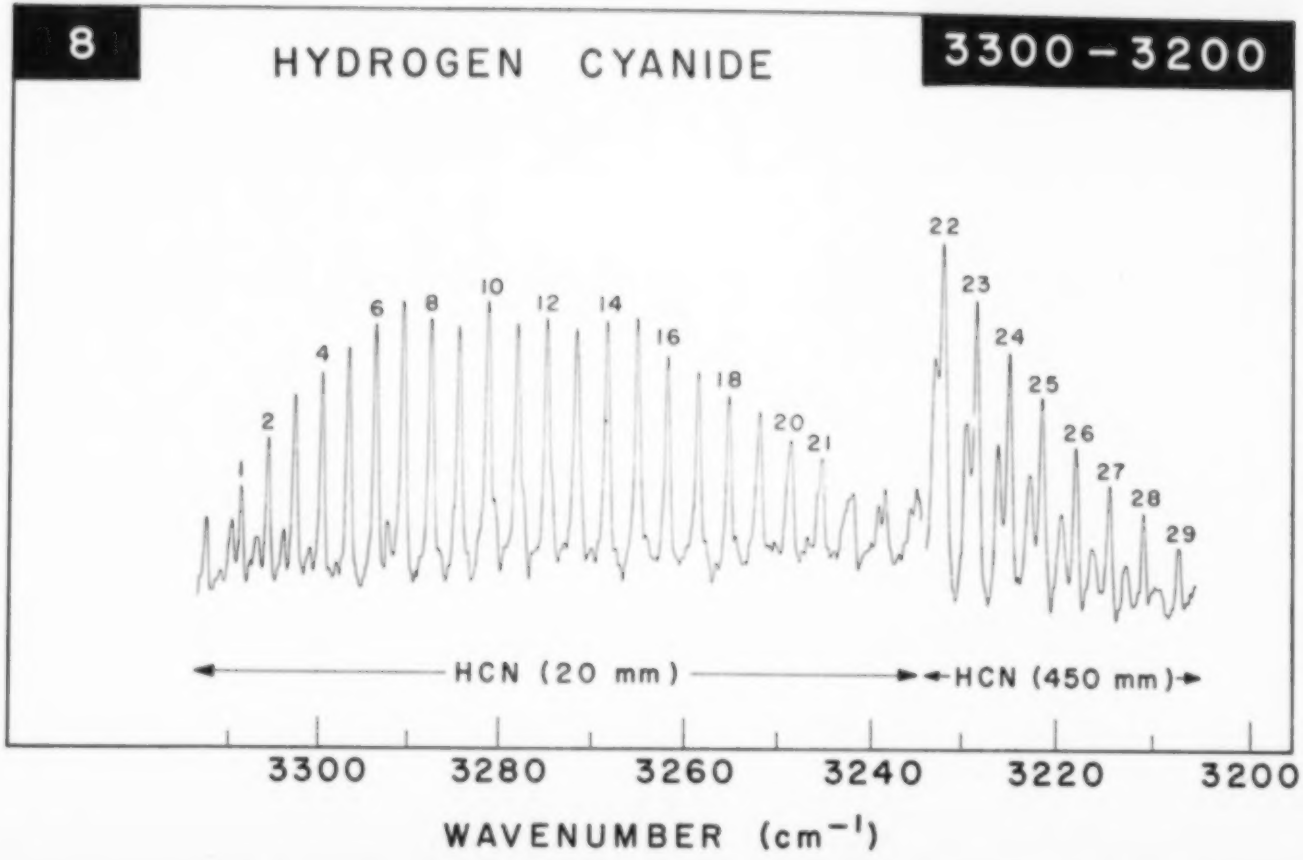
8
HYDROGEN CYANIDE
3300 – 3200
1
2
4
6
8
10
12
14
16
18
20
21
22
23
24
25
26
27
28
29
HCN (20 mm)
HCN (450 mm)
3300
3280
3260
3240
3220
3200
WAVENUMBER (cm⁻¹)

Chart 8. Hydrogen cyanide (20 mm) and (450 mm): 3300–3200 cm^{-1}

Hydrogen cyanide (20 mm)				*Hydrogen cyanide* (450 mm)	
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	3308·5†	13	3271·4_5†‡	22	3231·5
2	3305·5_5†	14	3268·2†‡	23	3228·0_5
3	3302·5_3†	15	3265·0†‡	24	3224·6
4	3299·5†‡	16	3261·7†‡	25	3221·1
5	3296·5†‡	17	3258·4_3†‡	26	3217·6
6	3293·4†‡	18	3255·1_5†‡	27	3214·0_3
7	3290·3_5†‡	19	3251·8†‡	28	3210·5
8	3287·2_3†‡	20	3248·5†‡	29	3206·9_5
9	3284·1†‡	21	3245·1†‡		
10	3281·0†‡				
11	3277·8†‡				
12	3274·6_5†‡				

Resolution tests: Line no. 10–line no. 11: 3·2 cm^{-1}
Line no. 26–line no. 27: 3·55 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 8A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

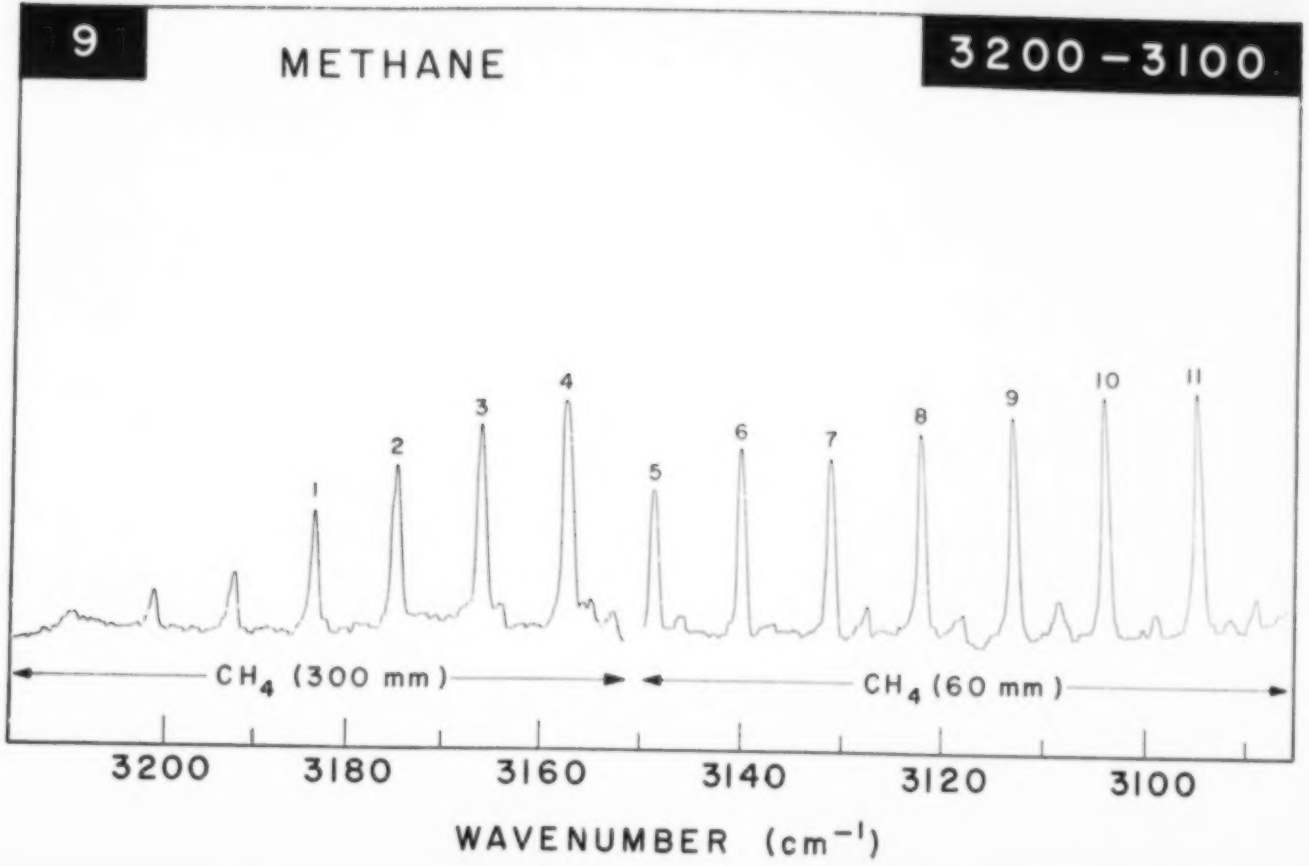
9
METHANE
3200 – 3100
1
2
3
4
5
6
7
8
9
10
11
CH4 (300 mm)
CH4 (60 mm)
3200
3180
3160
3140
3120
3100
WAVENUMBER (cm⁻¹)

Chart 9. Methane (300 mm) and (60 mm): 3200–3100 cm $^{-1}$

Methane (300 mm)		*Methane* (60 mm)	
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	3183·1	5	$3148{\cdot}9_5$†‡
2	$3174{\cdot}8_5$	6	3140·2†‡
3	3166·2†‡	7	3131·4†‡
4	3157·6†‡	8	$3122{\cdot}4_5$†‡
		9	3113·4†‡
		10	$3104{\cdot}3_5$†‡
		11	3095·2†‡

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 9A*).
[a] The estimated uncertainty does not exceed ±0·1 cm^{-1}.

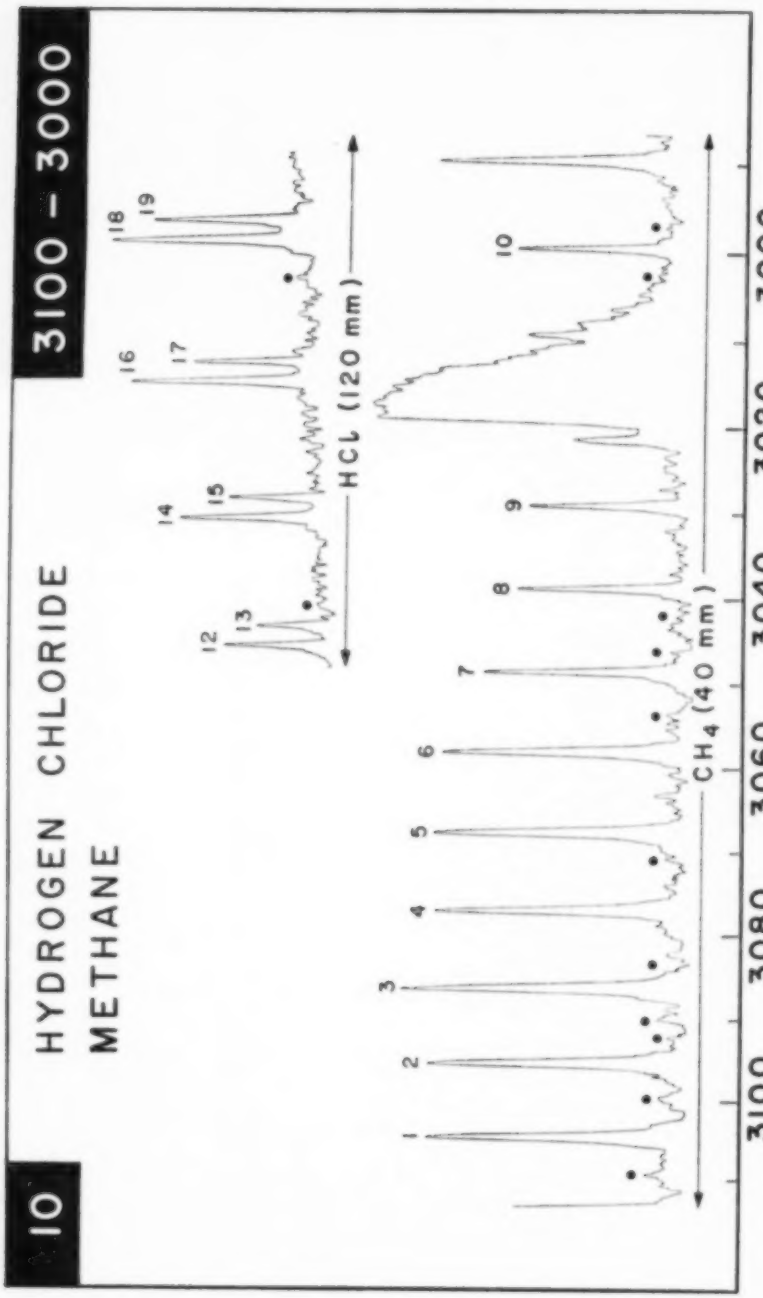
10
HYDROGEN CHLORIDE
METHANE
3100 – 3000
HCL (120 mm)
CH4 (40 mm)
WAVENUMBER (cm⁻¹)
3100
3080
3060
3040
3020
3000

Chart 10. Methane (40 mm) and hydrogen chloride (120 mm): 3100–3000 cm^{-1}

Methane (40 mm)		*Hydrogen chloride* (120 mm)			
Line no.	*Wavenumber*[a,c] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a,b,c] (vac.) (cm^{-1})		
1	$3104{\cdot}3_5$†‡	12	$3045{\cdot}0_5$†‡		
2	3095·2†‡	13	$3042{\cdot}7_5$†	(3044·5)	(±0·3 cm^{-1})
3	3086·0†‡	14	3030·1†‡		
4	$3076{\cdot}7_5$†‡	15	3027·8†	(3029·5)	(±0·3 cm^{-1})
5	3067·3†‡	16	$3014{\cdot}4_5$†‡		
6	3057·8†‡	17	$3012{\cdot}1_5$†	(3013·8$_5$)	(±0·3 cm^{-1})
7	$3048{\cdot}2_5$†‡	18	$2998{\cdot}0_5$†‡		
8	3038·6†‡	19	2995·8†	(2997·5)	(±0·3 cm^{-1})
9	$3028{\cdot}8_5$†‡				
10	2999·1†‡				
Resolution test: Line no. 16–line no. 17: 2·3 cm^{-1}					

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 10A*).
(a) Black circles on charts indicate positions of prominent water vapour lines.
(b) Under lower resolution the position of the more intense ($H^{35}Cl$) peak of each doublet is not significantly displaced provided the two peaks are separately resolved, as shown in *Charts 10A–14A*. If the resolution is further diminished, so that the lines blend, the main peak is displaced to lower wavenumber. If the blended line appears symmetrical, the position of the peak corresponds approximately to the weighted average of the positions of the two component lines, based on the $^{35}Cl/^{37}Cl$ abundance ratio of 0·75. These values are given in parentheses in the tables accompanying *Charts 10–14*.
(c) The estimated uncertainty does not exceed ±0·1 cm^{-1} unless otherwise indicated.

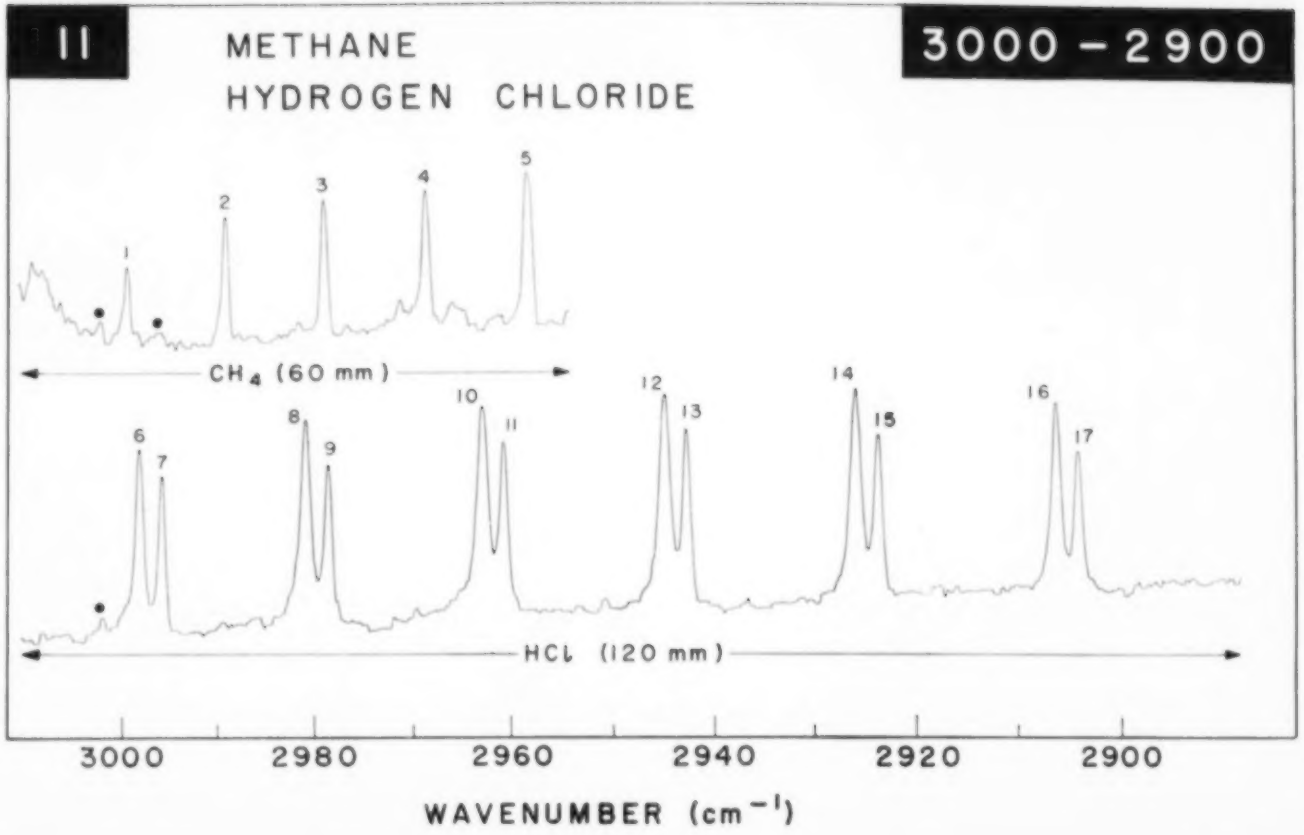
11
METHANE
HYDROGEN CHLORIDE
3000 – 2900
1
2
3
4
5
CH4 (60 mm)
6
7
8
9
10
11
12
13
14
15
16
17
HCl (120 mm)
3000
2980
2960
2940
2920
2900
WAVENUMBER (cm⁻¹)

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Chart 11. Methane (60 mm) and hydrogen chloride (120 mm): 3000–2900 cm^{-1}

Methane (60 mm)		*Hydrogen Chloride* (120 mm)	
Line no.	*Wavenumber*[a,b,c] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a,b,c] (vac.) (cm^{-1})
1	2999·1†‡	6	$2998{\cdot}0_b$†‡
2	2989·0†‡	7	$2995{\cdot}8$† (2997·5) (±0·3 cm^{-1})
3	2979·0†‡	8	2981·0†‡
4	$2968{\cdot}6_b$†‡	9	$2978{\cdot}7_b$† (2980·4$_b$) (±0·3 cm^{-1})
5	$2958{\cdot}2_b$†‡	10	2963·3†‡
		11	2961·1† (2962·7$_b$) (±0·3 cm^{-1})
		12	$2944{\cdot}9_b$†‡
		13	$2942{\cdot}7_b$† (2944·4) (±0·3 cm^{-1})
		14	$2925{\cdot}9_b$†‡
		15	$2923{\cdot}7_b$† (2925·3$_b$) (±0·3 cm^{-1})
		16	$2906{\cdot}2_b$†‡
		17	$2904{\cdot}1_b$† (2905·7$_b$) (±0·3 cm^{-1})

Resolution tests: Line no. 16–line no. 17: 2·1 cm^{-1}
Line no. 6–line no. 7: 2·25 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 11A*), see also footnote (b) to *Chart 10*.
(a) See footnote (b) to *Chart 10*.
(b) Black circles indicate positions of prominent atmospheric water vapour lines.
(c) The estimated uncertainty does not exceed ±0·1 cm^{-1} unless otherwise indicated.

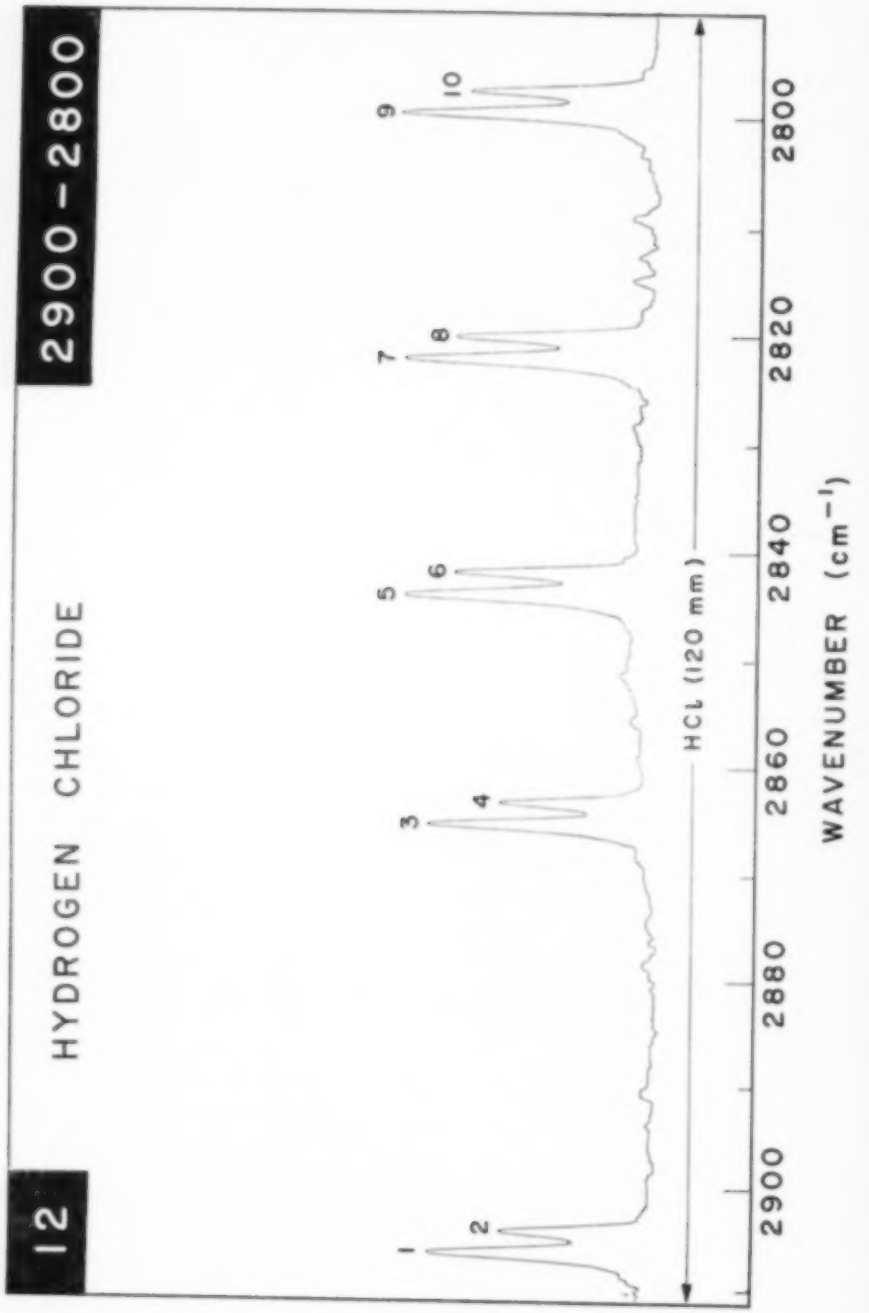
12
HYDROGEN CHLORIDE
2900-2800
HCl (120 mm)
1
2
3
4
5
6
7
8
9
10
2900
2880
2860
2840
2820
2800
WAVENUMBER (cm⁻¹)

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Chart 12. Hydrogen chloride (120 mm): 2900–2800 cm^{-1}

Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})		
1	$2906{\cdot}2_5$†‡		
2	$2904{\cdot}1_5$†	($2905{\cdot}7_5$)	($\pm 0{\cdot}3$ cm^{-1})
3	2865·1†‡		
4	$2863{\cdot}0_5$†	(2864·6)	($\pm 0{\cdot}3$ cm^{-1})
5	$2843{\cdot}6_5$†‡		
6	2841·6†	($2843{\cdot}1_5$)	($\pm 0{\cdot}3$ cm^{-1})
7	2821·6†‡		
8	2819·6†	(2821·1)	($\pm 0{\cdot}3$ cm^{-1})
9	$2798{\cdot}9_5$†‡		
10	2797·0†	($2798{\cdot}4_5$)	($\pm 0{\cdot}3$ cm^{-1})

Resolution tests: Line no. 9–line no. 10: ▶95 cm^{-1}
Line no. 1–line no. 2: 2·1 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 12A*), see also footnote (b) to *Chart 10*.
(a) See footnote (b) to *Chart 10*.
(b) The estimated uncertainty does not exceed $\pm 0{\cdot}1$ cm^{-1} unless otherwise indicated.

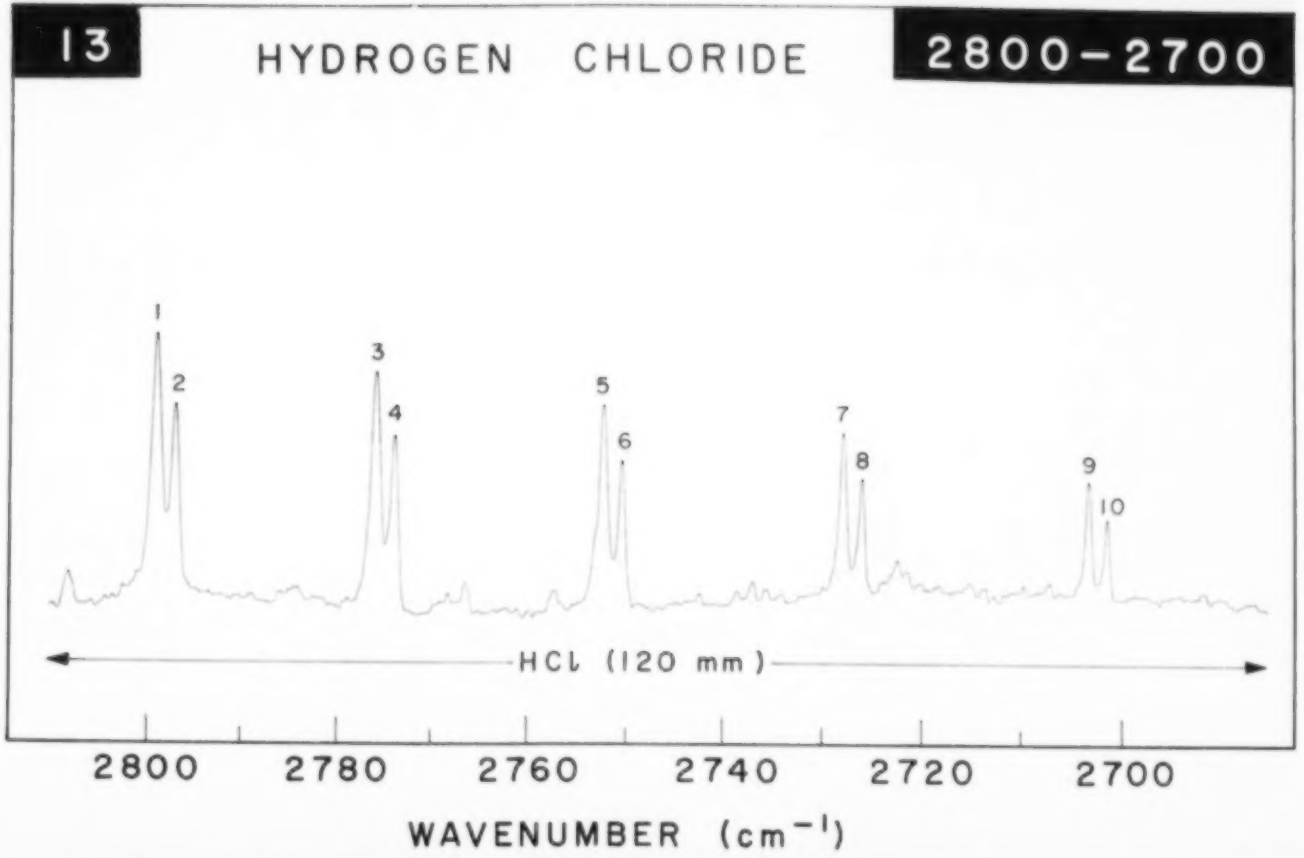
13
HYDROGEN CHLORIDE
2800–2700
1
2
3
4
5
6
7
8
9
10
HCl (120 mm)
2800
2780
2760
2740
2720
2700
WAVENUMBER (cm⁻¹)

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Chart 13. Hydrogen chloride (120 mm): 2800–2700 cm^{-1}

Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})		
1	2798·9$_5$†‡		
2	2797·0†	(2798·4$_5$)	(±0·3 cm^{-1})
3	2775·8†‡		
4	2773·8$_5$†	(2775·3)	(±0·3 cm^{-1})
5	2752·0$_5$†‡		
6	2750·1$_5$†	(2751·6)	(±0·3 cm^{-1})
7	2727·8†‡		
8	2725·9$_5$†	(2727·3$_5$)	(±0·3 cm^{-1})
9	2703·0$_5$†‡		
10	2701·2†	(2702·6)	(±0·3 cm^{-1})

Resolution tests: Line no. 9–line no. 10; 1·85 cm^{-1}
Line no. 1–line no. 2; 1·95 cm^{-1}

† Part 1 calibration line.
‡ Suitable for use under lower resolution (*Chart 13A*), see also footnote (b) to *Chart 10*.
(a) See footnote (b) to *Chart 10*.
(b) The estimated uncertainty does not exceed ±0·1 cm^{-1} unless otherwise indicated.

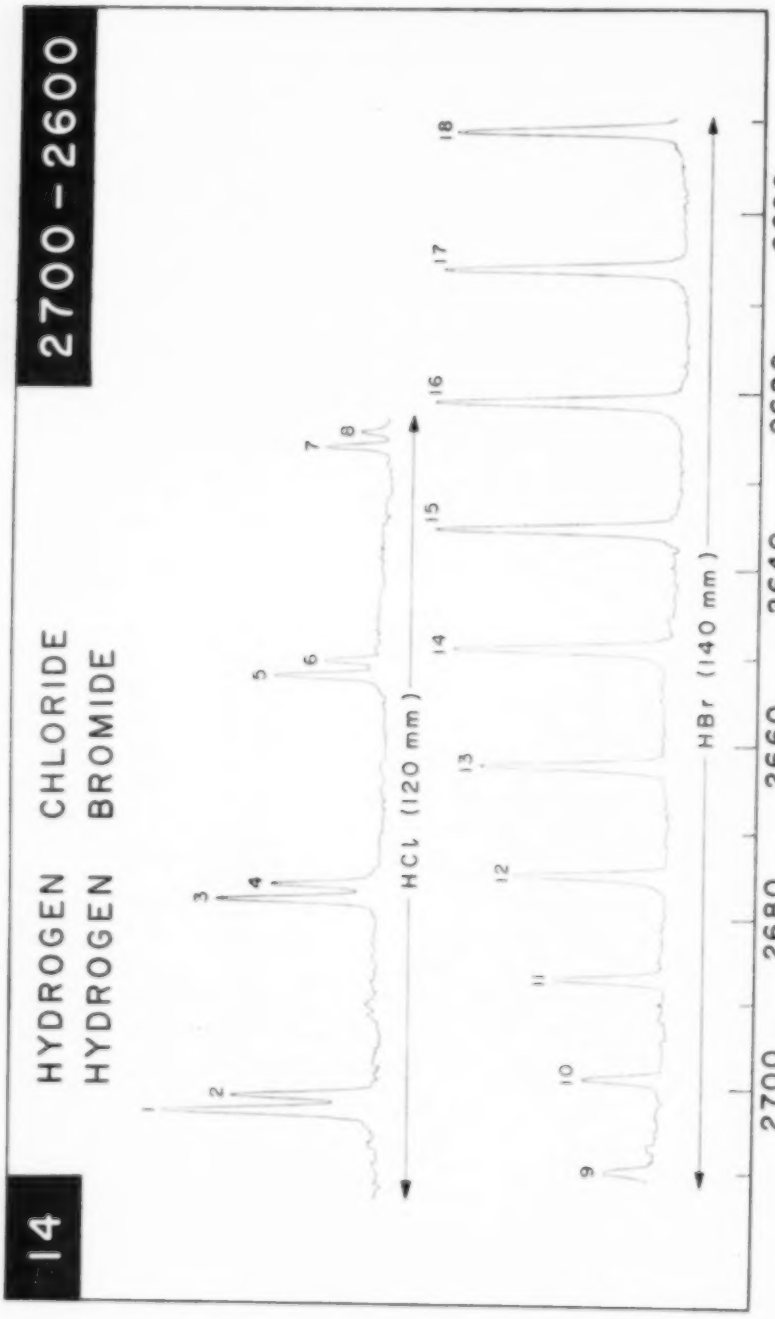
14
HYDROGEN CHLORIDE
HYDROGEN BROMIDE
2700 - 2600
HCl (120 mm)
HBr (140 mm)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
2700
2680
2660
2640
2620
2600
WAVENUMBER (cm⁻¹)

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Chart 14. Hydrogen chloride (120 mm) and hydrogen bromide (140 mm): 2700–2600 cm^{-1}

Hydrogen chloride (120 mm)			*Hydrogen bromide* (140 mm)	
Line no.	*Wavenumber*[a, b] (vac.) (cm^{-1})		*Line no.*	*Wavenumber*[b, c] (vac.) (cm^{-1})
1	$2703{\cdot}0_5$†‡		9	$2710{\cdot}0_5$†‡
2	2701·2†	($2702{\cdot}5_5$) ($\pm 0{\cdot}3$ cm^{-1})	10	2698·9†‡
3	$2677{\cdot}7_5$†‡		11	2687·2†‡
4	$2675{\cdot}9_5$†	($2677{\cdot}3$) ($\pm 0{\cdot}3$ cm^{-1})	12	$2674{\cdot}9_5$†‡
5	2652·0†‡		13	2662·2†‡
6	$2650{\cdot}2_5$†	($2651{\cdot}5_5$) ($\pm 0{\cdot}3$ cm^{-1})	14	2648·9†‡
7	2625·7		15	2635·1†‡
8	2624·0	—	16	2620·8†‡
			17	$2606{\cdot}0_5$†‡
			18	$2590{\cdot}7_5$†‡

Resolution tests:
Line no. 18 unresolved doublet spacing is 0·39 cm^{-1}
Line no. 12 unresolved doublet spacing is 0·40 cm^{-1}
Line no. 7–line no. 8: 1·7 cm^{-1}
Line no. 1–line no. 2: 1·85 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 14A*), see also footnote (b) to *Chart 10*.
(a) See footnote (b) to *Chart 10*.
(b) The estimated uncertainty does not exceed $\pm 0{\cdot}1$ cm^{-1} unless otherwise indicated.
(c) The lines are blends of two components from $H^{35}Br$ and $H^{37}Br$. Where the doublet is resolved the data from *Table 8* of Part I should be used.

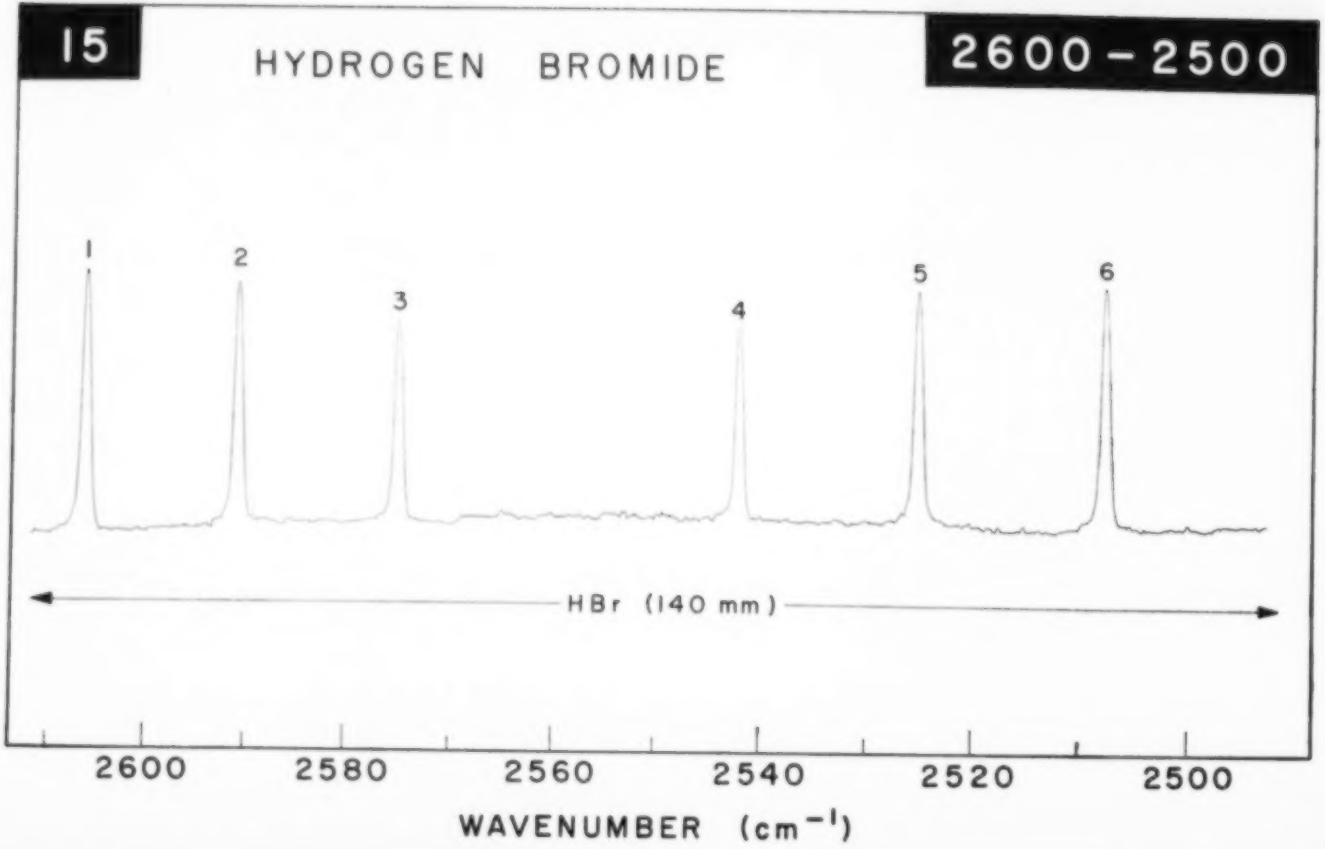
15
HYDROGEN BROMIDE
2600 – 2500
1
2
3
4
5
6
HBr (140 mm)
2600
2580
2560
2540
2520
2500
WAVENUMBER (cm⁻¹)

Chart 15. Hydrogen bromide (140 mm): 2600–2500 cm^{-1}

Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})
1	$2606{\cdot}0_5$†‡
2	$2590{\cdot}7_5$†‡
3	2575·0†‡
4	$2542{\cdot}0_5$†‡
5	2524·9†‡
6	2507·3†‡

Resolution tests: Line no. 6 unresolved doublet spacing is 0·36 cm^{-1}
Line no. 1 unresolved doublet spacing is 0·40 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 15A*).
(a) These lines are blends of two components from $H^{79}Br$ and $H^{81}Br$. Where the doublet is resolved the data from *Table 8* of Part I should be used.
(b) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

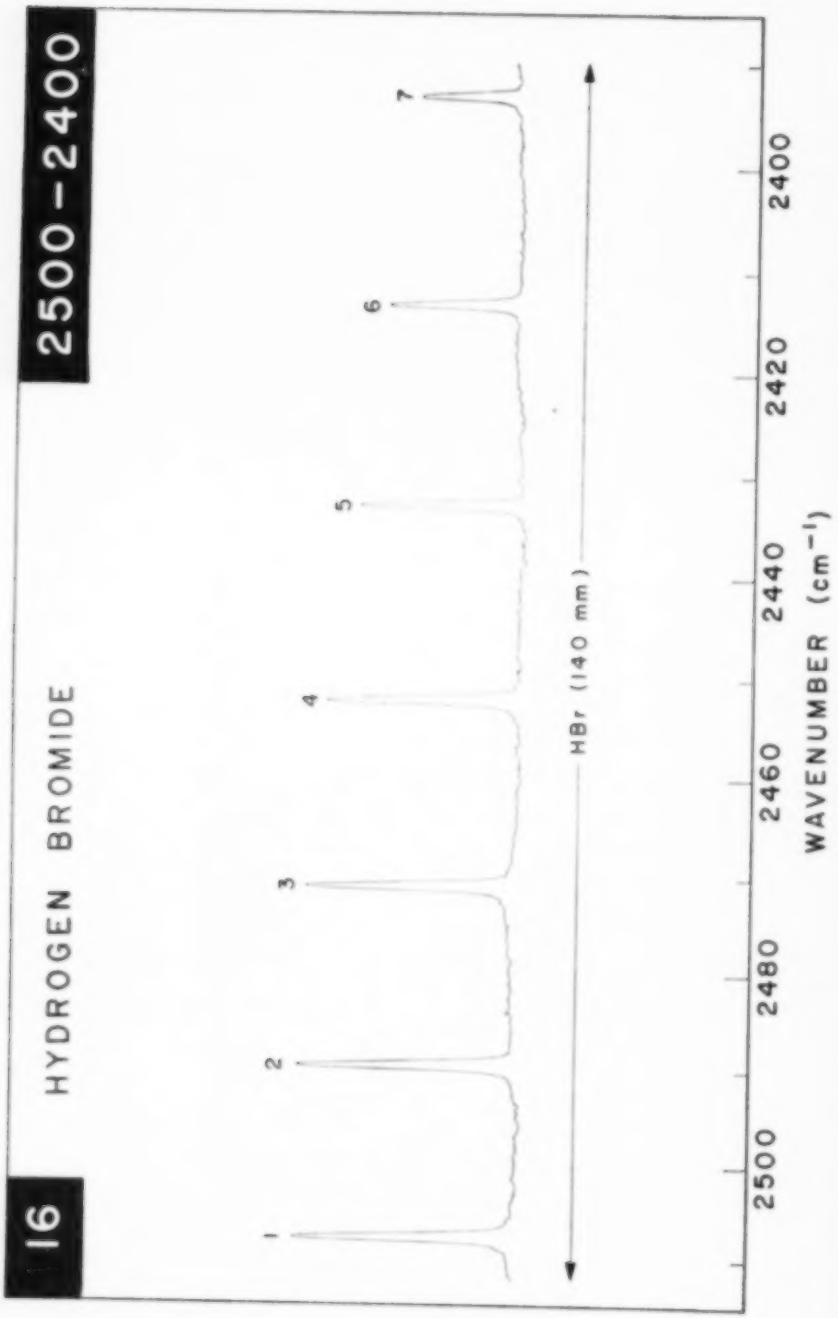
16
HYDROGEN BROMIDE
2500-2400
1
2
3
4
5
6
7
HBr (140 mm)
2500
2480
2460
2440
2420
2400
WAVENUMBER (cm⁻¹)

Chart 16. Hydrogen bromide (140 mm): 2500–2400 cm^{-1}

Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})
1	2507·3†‡
2	2489·2$_5$†‡
3	2470·8†‡
4	2451·9†‡
5	2432·6†‡
6	2412·9†‡
7	2392·8†‡

Resolution tests: Line no. 7 unresolved doublet spacing is 0·33 cm^{-1}
Line no. 1 unresolved doublet spacing is 0·36 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 16A*).
(a) These lines are blends of two components from $H^{79}Br$ and $H^{81}Br$. Where the doublet is resolved the data from *Table 8* of Part I should be used.
(b) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

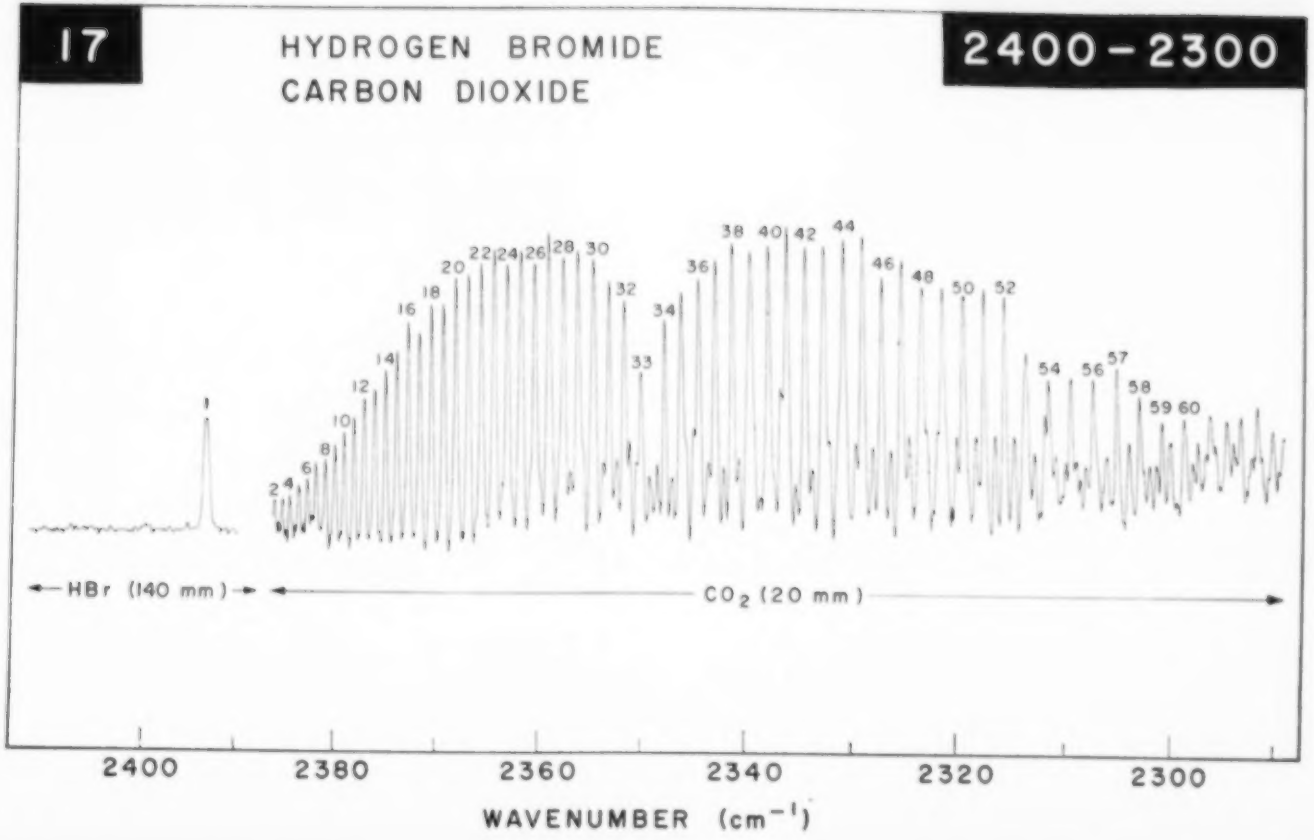
17
HYDROGEN BROMIDE
CARBON DIOXIDE
2400-2300
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 33 34 36 38 40 42 44 46 48 50 52 54 56 57 58 59 60
HBr (140 mm)
CO2 (20 mm)
2400 2380 2360 2340 2320 2300
WAVENUMBER (cm-1)

Chart 17. Hydrogen bromide (140 mm) and carbon dioxide (20 mm): 2400–2300 cm^{-1}

Hydrogen bromide (140 mm)		*Carbon dioxide* (20 mm)					
Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})
1	2392·8†‡	2	2385·8 (±0·2 cm^{-1})	22	2365·4†	42	2334·2†‡
		3	2385·0 (±0·2 cm^{-1})	23	2364·1$_5$†	43	2332·4†‡
		4	2384·2 (±0·2 cm^{-1})	24	2362·8$_5$†	44	2330·6†‡
		5	2383·4 (±0·2 cm^{-1})	25	2361·5†	45	2328·7$_5$†‡
		6	2382·5 (±0·2 cm^{-1})	26	2360·1$_5$†	46	2326·9†‡
		7	2381·6$_5$ (±0·2 cm^{-1})	27	2358·7$_5$†	47	2325·0†‡
		8	2380·7$_5$†	28	2357·3$_5$†	48	2323·1†‡
		9	2379·8†	29	2355·9$_5$†	49	2321·1$_5$†‡
		10	2378·8$_5$†	30	2354·5†	50	2319·2†‡
		11	2377·9†	31	2353·0†	51	2317·2†‡
		12	2376·8$_5$†	32	2351·5†	52	2315·2†‡
		13	2375·8$_5$†	33	2349·9$_5$†	53	2313·2†‡
		14	2374·8†	34	2347·6†	54	2311·1†‡
		15	2373·7†	35	2346·0†	55	2309·0$_5$†‡
		16	2372·6†	36	2344·4†	56	2306·9$_5$†‡
		17	2371·4$_5$†	37	2342·7$_5$†	57	2304·8$_5$†‡
		18	2370·3†	38	2341·1†	58	2302·7†‡
		19	2369·1†	39	2339·4†‡	59	2300·5
		20	2367·9†	40	2337·7†	60	2298·3‡
		21	2366·7†	41	2335·9$_5$†		

Resolution tests: Line no. 10–line no. 11: 0·95 cm^{-1}
Line no. 48–line no. 49: 1·95 cm^{-1}

† Part 1 calibration line.
‡ Suitable for use under lower resolution (*Chart 17A*). The weak hydrogen bromide line at 2372·3 cm^{-1} can be used as an additional calibration point.
(a) See footnote (a) to *Chart 15*.
(b) The estimated uncertainty does not exceed ±0·1 cm^{-1} unless otherwise indicated.

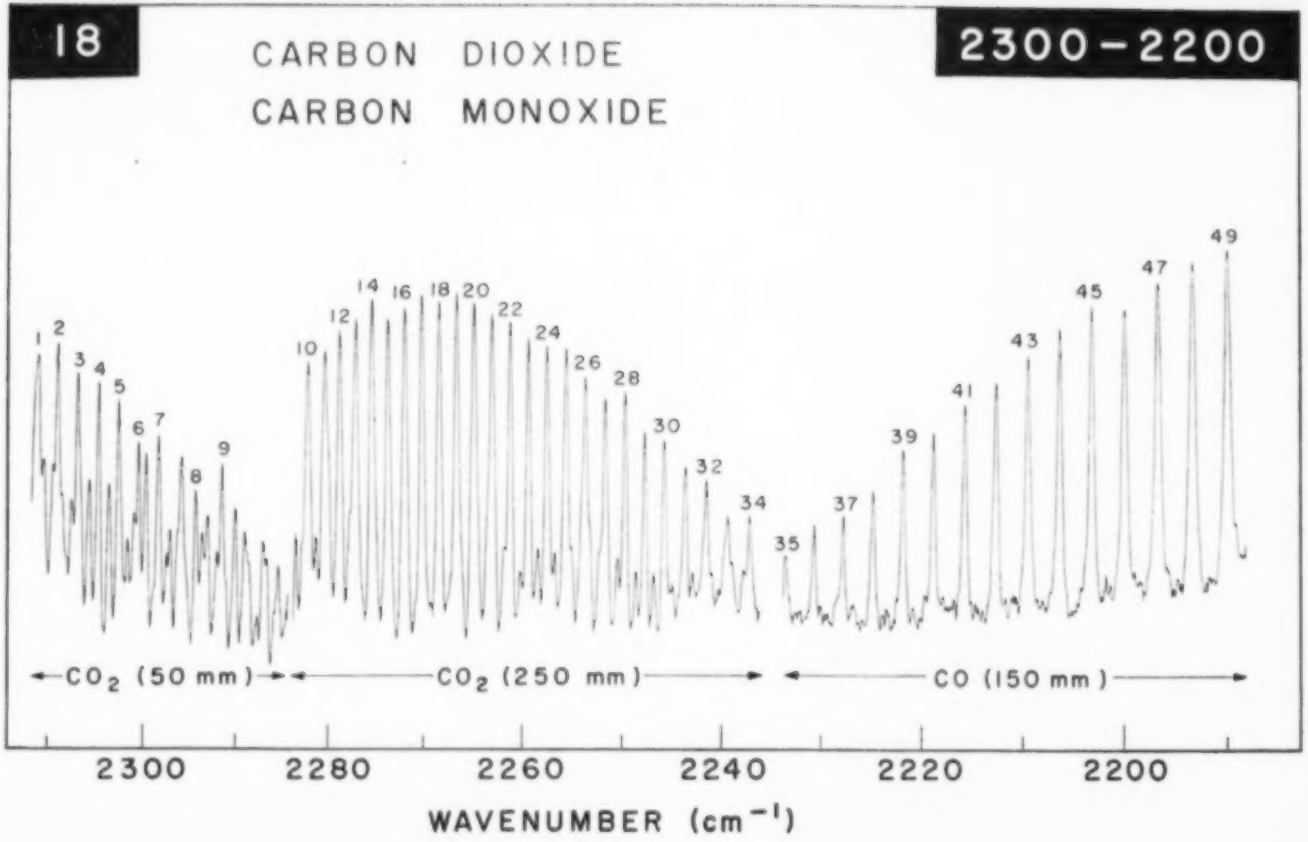
18
CARBON DIOXIDE
CARBON MONOXIDE
2300-2200
1 2 3 4 5 6 7 8 9 10 12 14 16 18 20 22 24 26 28 30 32 34 35 37 39 41 43 45 47 49
CO2 (50 mm)
CO2 (250 mm)
CO (150 mm)
2300 2280 2260 2240 2220 2200
WAVENUMBER (cm-1)

Chart 18. Carbon dioxide (50 mm), carbon dioxide (250 mm) and carbon monoxide (150 mm): 2300–2200 cm^{-1}

Carbon dioxide (50 mm)		*Carbon dioxide* (250 mm)		*Carbon monoxide* (150 mm)	
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	2311·1†‡	10	2281·9$_5$†‡	35	2233·3$_5$†
		11	2280·3$_5$†	36	2230·5$_5$†
2	2309·0$_5$†‡	12	2278·7†	37	2227·6$_5$†‡
		13	2277·1†	38	2224·7†‡
3	2306·9$_5$†‡	14	2275·4†‡	39	2221·7$_5$†‡
		15	2273·7$_5$†‡	40	2218·7$_5$†‡
4	2304·8$_5$†‡	16	2272·0$_5$†‡	41	2215·7†‡
		17	2270·3†‡	42	2212·6†‡
5	2302·7†‡	18	2268·5$_5$†‡	43	2209·5†‡
		19	2266·7$_5$†‡	44	2206·3$_5$†‡
6	2300·5†‡	20	2264·9$_5$†‡	45	2203·1$_5$†‡
		21	2263·1$_5$†‡	46	2199·9$_5$†‡
7	2298·3‡ (±0·2 cm^{-1})	22	2261·3†‡	47	2196·6$_5$†‡
		23	2259·4†‡	48	2193·3$_5$†‡
8	2294·4$_5$†	24	2257·5†‡	49	2190·0†‡
		25	2255·6†‡		
9	2291·6†	26	2253·6$_5$†‡		
		27	2251·7†‡		
		28	2249·7†‡		
		29	2247·7†‡		
		30	2245·6‡		
		31	2243·5$_5$‡		
		32	2241·4$_5$‡		
		33	2239·4‡		
		34	2237·2$_5$‡		

Resolution tests: Line no. 16–line no. 17: 1·75 cm^{-1}
Line no. 46–line no. 47: 3·3 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 18A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1} unless otherwise indicated.

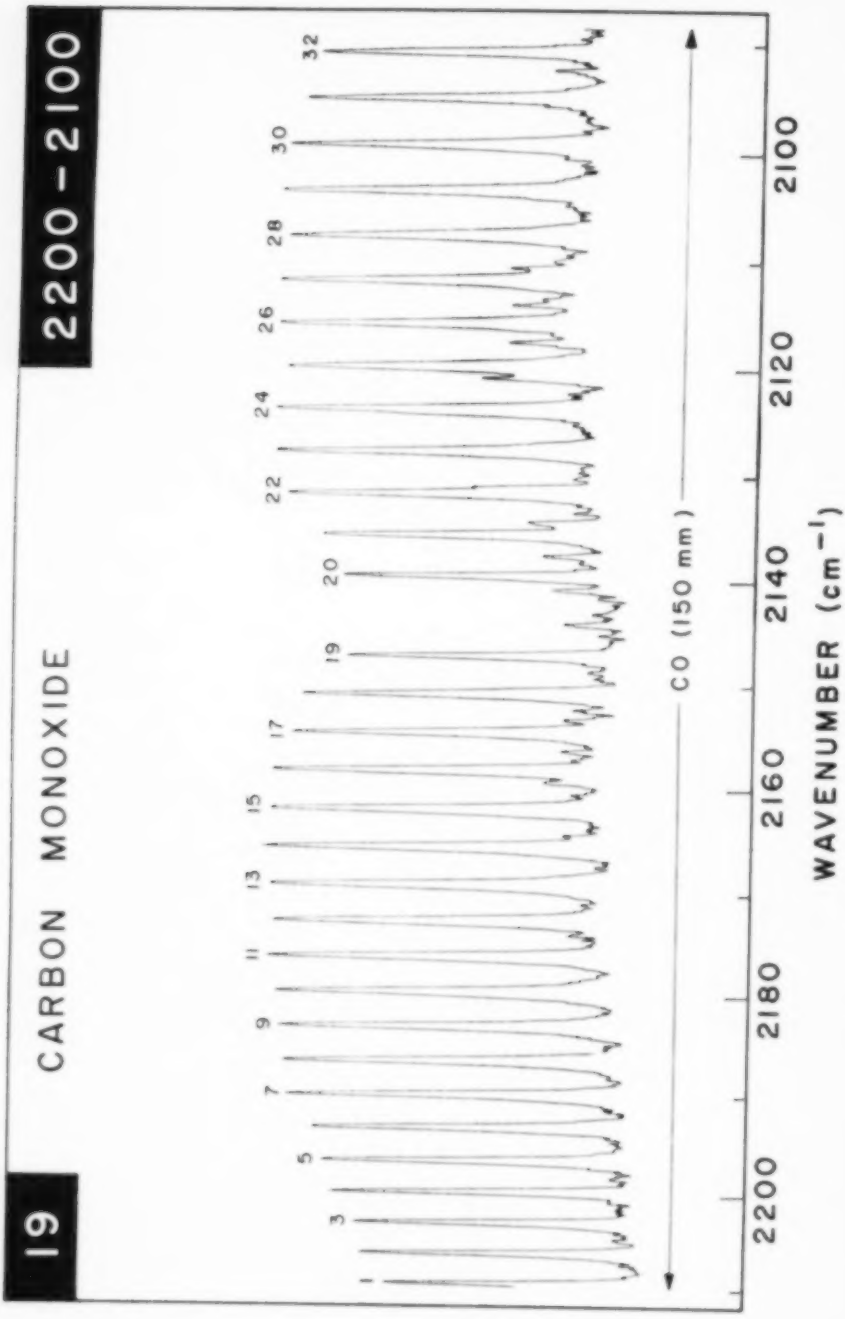
19
CARBON MONOXIDE
2200-2100
1
3
5
7
9
11
13
15
17
19
20
22
24
26
28
30
32
CO (150 mm)
2200
2180
2160
2140
2120
2100
WAVENUMBER (cm⁻¹)

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Chart 19. Carbon monoxide (150 mm): 2200–2100 cm^{-1}

Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	2209·5†‡	17	2154·6†‡
2	$2206{\cdot}3_5$†‡	18	$2150{\cdot}8_5$†‡
3	$2203{\cdot}1_5$†‡	19	2147·1†‡
4	$2199{\cdot}9_5$†‡	20	$2139{\cdot}4_5$†‡
5	$2196{\cdot}6_5$†‡	21	$2135{\cdot}5_5$†‡
6	$2193{\cdot}3_5$†‡	22	$2131{\cdot}6_5$†‡
7	2190·0†‡	23	2127·7†‡
8	$2186{\cdot}6_5$†‡	24	2123·7†‡
9	$2183{\cdot}2_5$†‡	25	2119·7†‡
10	$2179{\cdot}7_5$†‡	26	$2115{\cdot}6_5$†‡
11	2176·3†‡	27	$2111{\cdot}5_5$†‡
12	$2172{\cdot}7_5$†‡	28	2107·4†‡
13	2169·2†‡	29	$2103{\cdot}2_5$†‡
14	2165·6†‡	30	2099·1†‡
15	$2161{\cdot}9_5$†‡	31	$2094{\cdot}8_5$†‡
16	2158·3†‡	32	2090·6†‡

Resolution tests: Line no. 7–line no. 8: 3·35 cm^{-1}
Line no. 30–line no. 31: 4·25 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 19A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

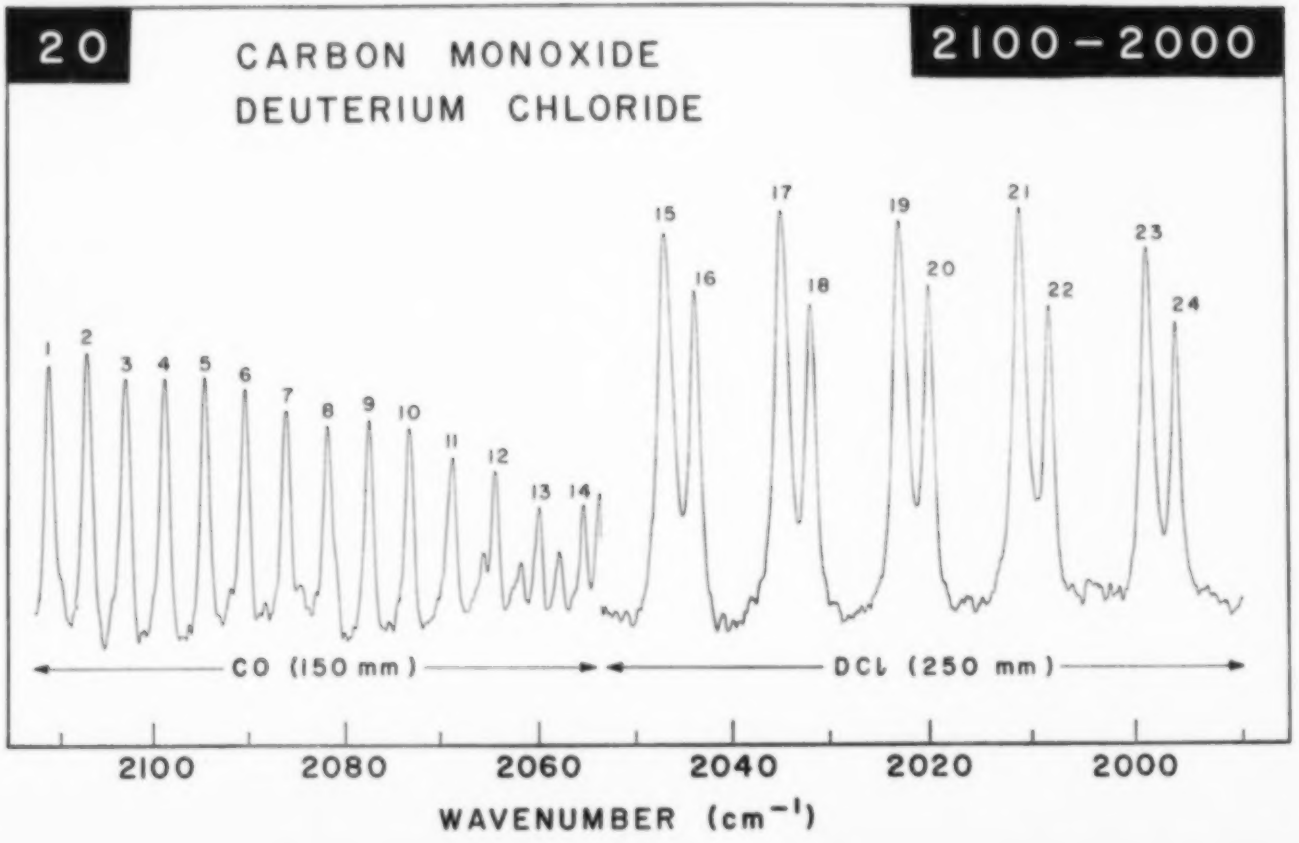
20
CARBON MONOXIDE
DEUTERIUM CHLORIDE
2100 – 2000
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
CO (150 mm)
DCl (250 mm)
2100
2080
2060
2040
2020
2000
WAVENUMBER (cm⁻¹)

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Chart 20. Carbon monoxide (150 mm) and deuterium chloride (250 mm): 2100–2000 cm^{-1}

Carbon monoxide (150 mm)		*Deuterium chloride* (250 mm)			
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a,b] (vac.) (cm^{-1})		
1	2111·5_5†‡	15	2046·6†		
2	2107·4†‡	16	2043·7_5†	(2045·9)	(±0·3 cm^{-1})
3	2103·2_5†‡	17	2034·9_5†		
4	2099·1†‡	18	2032·1†	(2034·2_5)	(±0·3 cm^{-1})
5	2094·8_5†‡	19	2023·1†‡		
6	2090·6†‡	20	2020·3†	(2022·4)	(±0·3 cm^{-1})
7	2086·3†‡	21	2011·0_5†‡		
8	2082·0†‡	22	2008·2_5†	(2010·3_5)	(±0·3 cm^{-1})
9	2077·6_5†‡	23	1998·7_5†‡		
10	2073·2_5†‡	24	1996·0_5†	(1998·1)	(±0·3 cm^{-1})
11	2068·8_5†‡				
12	2064·4†‡				
13	2059·9†				
14	2055·4†				

Resolution tests: Line no. 23–line no. 24: 2·7 cm^{-1}
Line no. 2–line no. 3: 4·15 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 20A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1} unless otherwise indicated.
(b) Under lower resolution the position of the more intense ($D^{35}Cl$) peak of each doublet is not significantly displaced provided the two peaks are separately resolved, as shown in *Charts 20A* and *21A*. If the resolution is further diminished, so that the lines blend, the main peak is displaced to lower wavenumber. If the blended line appears symmetrical, the position of the peak corresponds approximately to the weighted average of the positions of the two component lines, based on the $^{35}Cl/^{37}Cl$ abundance ratio of 0·75. These values are given in parentheses in the tables accompanying *Charts 20* and *21*.

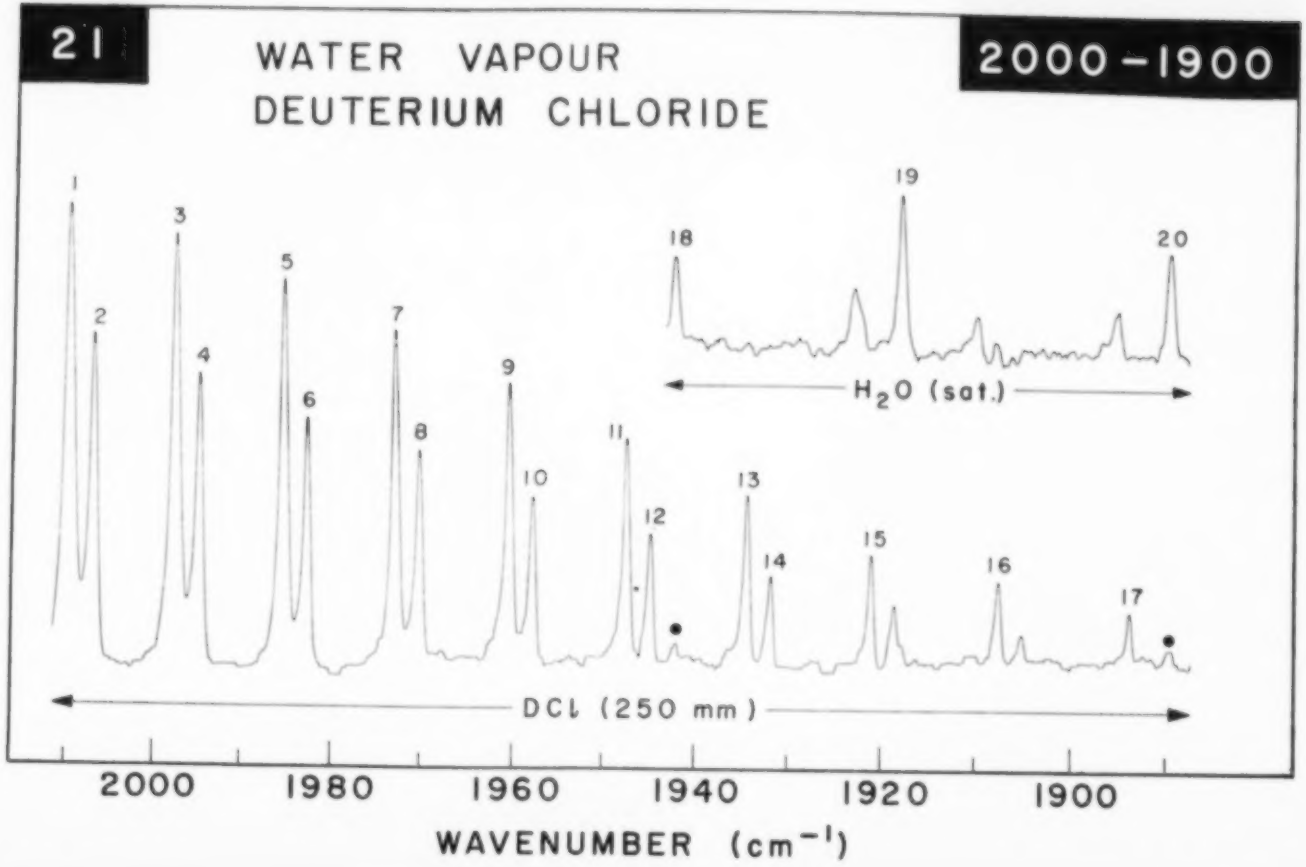
21
WATER VAPOUR
DEUTERIUM CHLORIDE
2000–1900
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
H_2O (sat.)
DCl (250 mm)
2000
1980
1960
1940
1920
1900
WAVENUMBER (cm^{-1})

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Chart 21. Deuterium chloride (250 mm) and water vapour (saturated): 2000–1900 cm^{-1}

Deuterium chloride (250 mm)		*Water vapour (saturated)*	
Line no.	*Wavenumber*[a,b,c] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[c] (vac.) (cm^{-1})
1	$2011{\cdot}0_5$†‡	18	1942·6‡
2	$2008{\cdot}2_5$† ($2010{\cdot}3_5$) ($\pm 0{\cdot}3$ cm^{-1})		
3	$1998{\cdot}7_5$†‡	19	$1918{\cdot}0_5$‡
4	$1996{\cdot}0_5$† (1998·1) ($\pm 0{\cdot}3$ cm^{-1})		
5	$1986{\cdot}3$†‡	20	1889·6†‡
6	$1983{\cdot}6_5$† ($1985{\cdot}6_5$) ($\pm 0{\cdot}3$ cm^{-1})		
7	$1973{\cdot}6_5$†‡		
8	1971·0† (1973·0) ($\pm 0{\cdot}3$ cm^{-1})		
9	1960·8†‡		
10	1958·2† ($1960{\cdot}1_5$) ($\pm 0{\cdot}3$ cm^{-1})		
11	$1947{\cdot}7_5$†‡		
12	$1945{\cdot}2$† ($1947{\cdot}1_5$) ($\pm 0{\cdot}3$ cm^{-1})		
13	$1934{\cdot}5_5$†‡		
14	$1932{\cdot}0_5$† ($1933{\cdot}9_5$) ($\pm 0{\cdot}3$ cm^{-1})		
15	$1921{\cdot}1_5$†‡ ($1920{\cdot}5_5$) ($\pm 0{\cdot}3$ cm^{-1})		
16	1907·6†‡ (1907·0) ($\pm 0{\cdot}3$ cm^{-1})		
17	$1893{\cdot}8_5$‡ ($\pm 0{\cdot}2$ cm^{-1})		

Resolution tests: Line no. 13–line no. 14: 2·5 cm^{-1}
Line no. 1–line no. 2: 2·8 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 21A*). See also footnote (a) to *Chart 20*.
(a) See footnote (a) to *Chart 20*.
(b) Black circles indicate positions of prominent atmospheric water vapour lines.
(c) The estimated uncertainty does not exceed $\pm 0{\cdot}1$ cm^{-1} unless otherwise indicated.

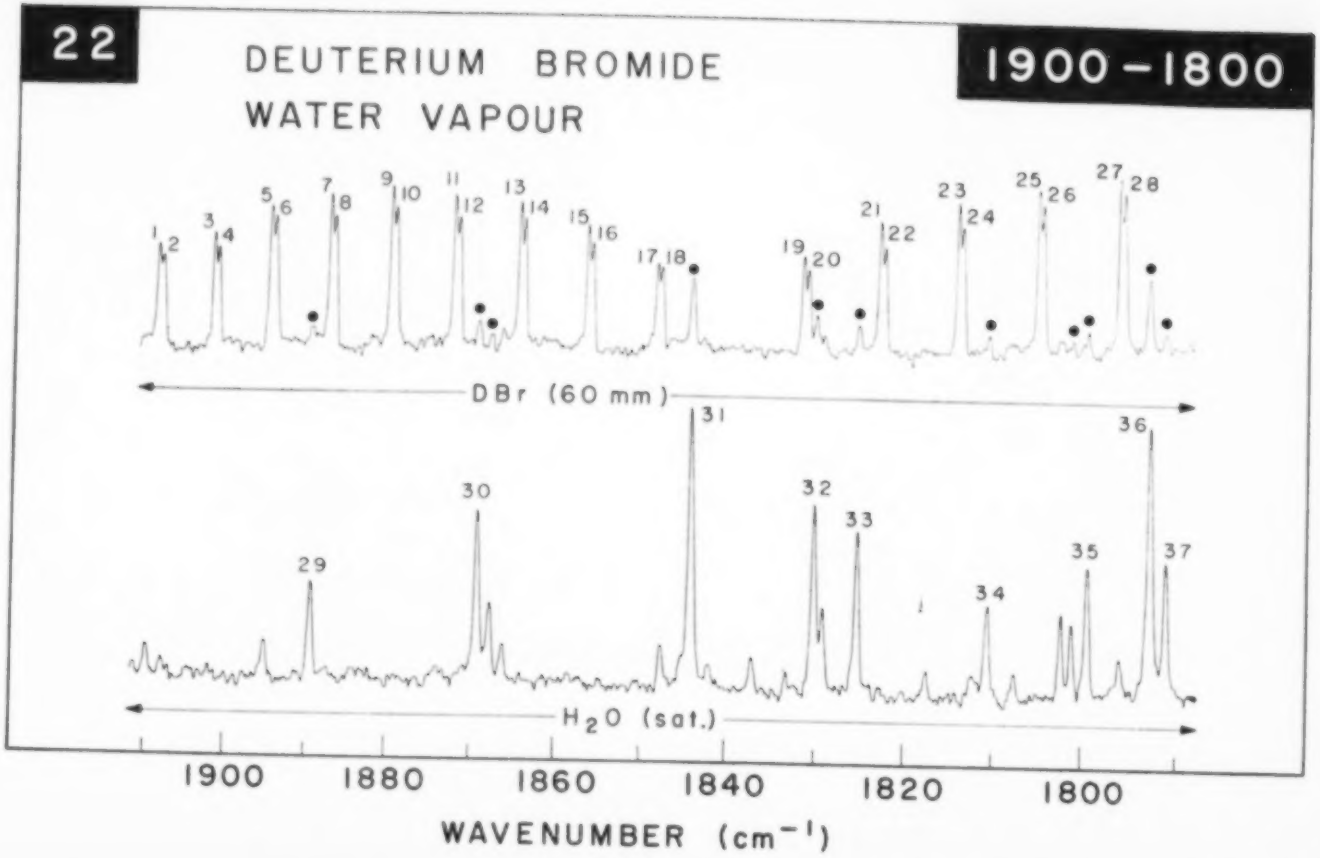
22
DEUTERIUM BROMIDE
WATER VAPOUR
1900–1800
DBr (60 mm)
H2O (sat.)
1900
1880
1860
1840
1820
1800
WAVENUMBER (cm⁻¹)

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Chart 22. Deuterium bromide (60 mm) and water vapour (saturated): 1900–1800 cm^{-1}

Deuterium bromide (60 mm)				*Water vapour* (*saturated*)	
Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a,b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[d] (vac.) (cm^{-1})
1	1908·7$_s$† (1908·4$_s$)	15	1856·5$_s$† (1856·2$_s$)	29	1889·6†‡
2	1908·1†	16	1856·0†	30	1869·3$_s$†
3	1901·8$_s$† (1901·5$_s$)	17	1848·4† (1848·1$_s$)	31	1844·2$_s$‡(c)
4	1901·2$_s$†	18	1847·9†	32	1830·2$_s$‡
5	1894·7$_s$† (1894·4$_s$)	19	1831·5$_s$† (1831·3)	33	1825·2$_s$†
6	1894·1$_s$†	20	1831·0$_s$†	34	1810·6$_s$†
7	1887·4$_s$† (1887·1$_s$)	21	1822·9† (1822·6$_s$)	35	1799·6†
8	1886·9†	22	1822·4†	36	1792·6$_s$‡
9	1880·0† (1879·7$_s$)	23	1814·1† (1813·8$_s$)	37	1790·9$_s$
10	1879·5†	24	1813·6†		
11	1872·3$_s$† (1872·1)	25	1805·1† (1804·8$_s$)		
12	1871·8†	26	1804·6†		
13	1864·5$_s$† (1864·2$_s$)	27	1795·9$_s$† (1795·7$_s$)		
14	1864·0†	28	1795·5†		

Resolution tests: Line no. 27–line no. 28: 0·45 cm^{-1}
Line no. 1–line no. 2: 0·65 cm^{-1}
Line no. 36–line no. 37: 1·7 cm^{-1}

† Part I calibration lines.
‡ Suitable for use under lower resolution (*Chart 22A*), see also footnote (a) below.
(a) Where the D^{79}Br and D^{81}Br doublet is not resolved a mean value for the peak positions may be used (these figures are given in parentheses).
(b) Black circles indicate positions of prominent atmospheric water vapour lines.
(c) Blend of two component lines.
(d) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

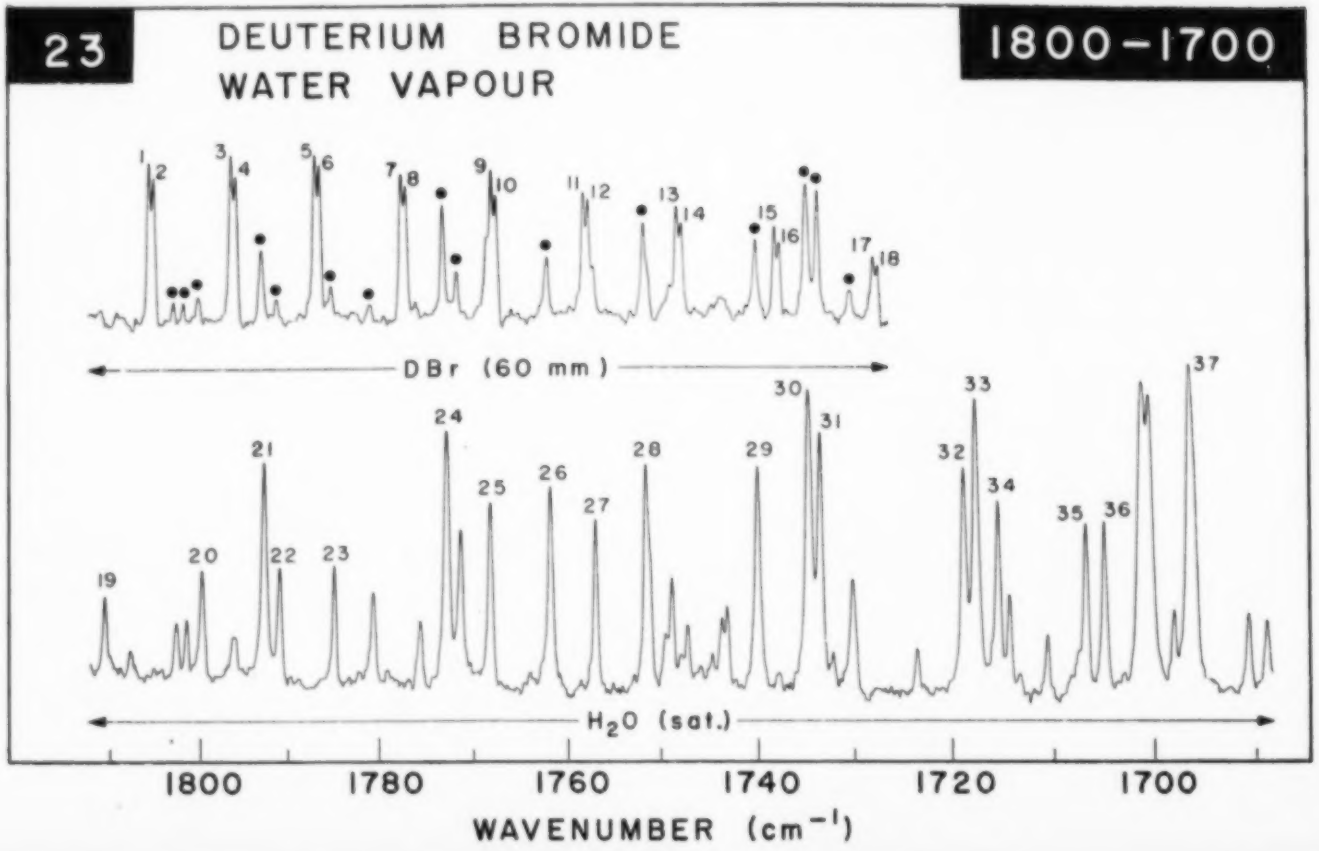
23
DEUTERIUM BROMIDE
WATER VAPOUR
1800–1700
DBr (60 mm)
H2O (sat.)
1800
1780
1760
1740
1720
1700
WAVENUMBER (cm-1)

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Chart 23. Deuterium bromide (60 mm) and water vapour (saturated): 1800–1700 cm^{-1}

Deuterium bromide (60 mm)			*Water vapour* (*saturated*)	
Line no.	*Wavenumber*[a,b] (vac.) (cm^{-1})		*Line no.*	*Wavenumber*[c] (vac.) (cm^{-1})
1	1805·1†		19	$1810{\cdot}6_b$†
2	1804·6†	(1804·8_b)	20	1799·6†
3	$1795{\cdot}9_b$†		21	$1792{\cdot}6_b$‡
4	1795·5†	(1795·7_b)	22	$1790{\cdot}9_b$
5	$1786{\cdot}6_b$†		23	$1784{\cdot}9_b$†‡
6	1786·2†	(1786·4)	24	$1772{\cdot}6_b$
7	1777·2†		25	$1768{\cdot}1_b$†
8	1776·7†	(1776·9_b)	26	1761·9‡
9	1767·6†		27	1756·8†‡
10	1767·1†	(1767·3_b)	28	$1751{\cdot}4_b$
11	$1757{\cdot}8_b$†		29	$1739{\cdot}8_b$‡
12	1757·4†	(1757·6)	30	$1734{\cdot}6_b$
13	$1747{\cdot}9_b$†		31	$1733{\cdot}4_b$
14	$1747{\cdot}4_b$†	(1747·7)	32	$1718{\cdot}6_b$
15	1737·9†		33	$1717{\cdot}4_b$‡
16	$1737{\cdot}4_b$†	(1737·6_b)	34	1715·2
17	1727·7†		35	$1706{\cdot}3_b$
18	$1727{\cdot}2_b$†	(1727·5)	36	1704·5
			37	$1695{\cdot}9_b$‡

Resolution tests: Line no. 11–line no. 12: 0·45 cm^{-1}
Line no. 30–line no. 31: 1·2 cm^{-1}
Line no. 21–line no. 22: 1·7 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 23A*), see also footnote (a) below.
(a) Where the $D^{79}Br$ and $D^{81}Br$ doublet is not resolved, a mean value for the peak positions may be used (these figures are given in parentheses).
(b) Black circles indicate positions of prominent atmospheric water vapour lines.
(c) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

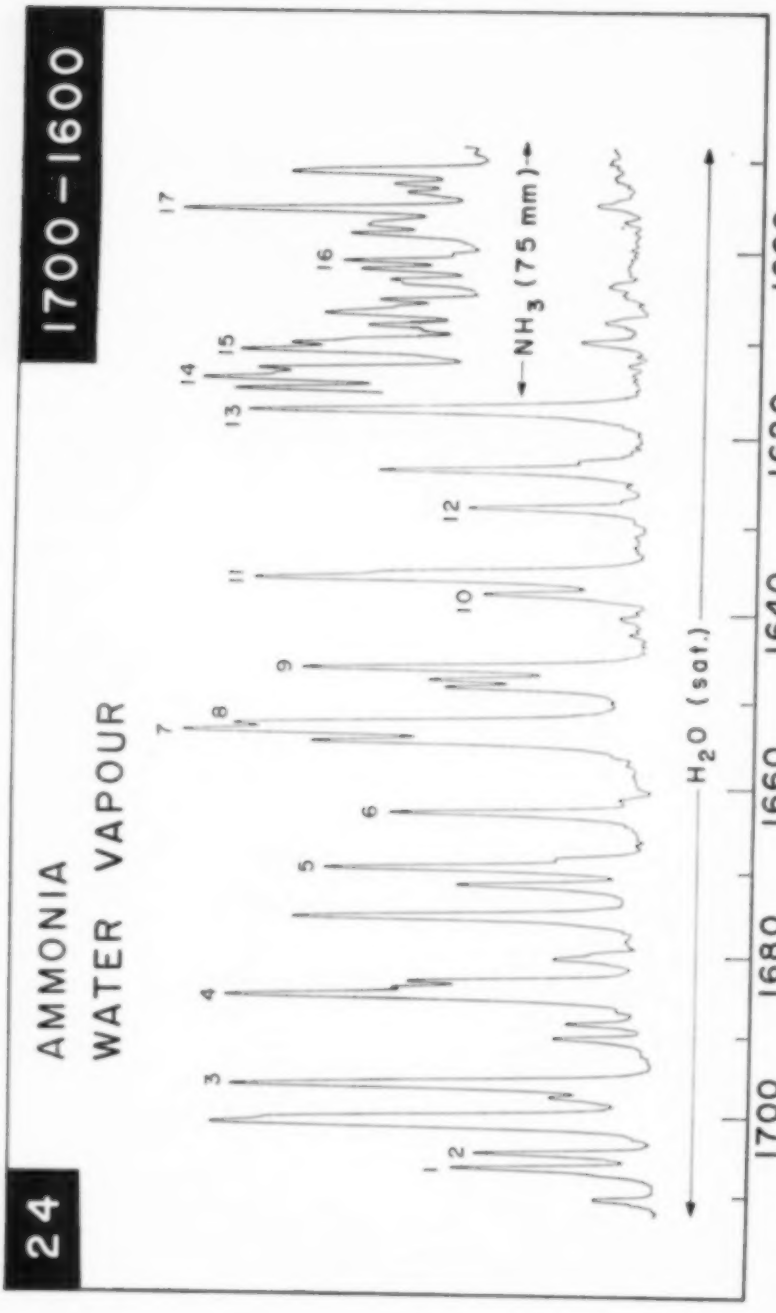
24
AMMONIA
WATER VAPOUR
1700–1600
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
NH_3 (75 mm)
H_2O (sat.)
1700 1680 1660 1640 1620 1600
WAVENUMBER (cm^{-1})

Chart 24. Water vapour (saturated) and ammonia (75 mm): 1700–1600 cm^{-1}

Water vapour (saturated)		*Ammonia* (75 mm)	
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	$1706{\cdot}3_b$	14	$1613{\cdot}3_b$ ($\pm 0{\cdot}2$ cm^{-1})
2	1704·5	15	$1610{\cdot}3_b$ ($\pm 0{\cdot}2$ cm^{-1})
3	$1695{\cdot}9_b$‡	16	1600·6 ($\pm 0{\cdot}2$ cm^{-1})
4	1684·9	17	$1594{\cdot}8_b$† ‡ ($\pm 0{\cdot}2$ cm^{-1})
5	$1669{\cdot}4_b$‡		
6	$1662{\cdot}8$† ‡		
7	$1653{\cdot}3_b$‡		
8	$1652{\cdot}4_b$		
9	1646·0		
10	$1637{\cdot}5_b$†		
11	1635·6‡		
12	1627·8†		
13	1616·7† ‡		

Resolution tests: Line no. 7–line no. 8: 0·9 cm^{-1}
Line no. 1–line no. 2: 1·85 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 24A*).
(a) The estimated uncertainty does not exceed $\pm 0{\cdot}1$ cm^{-1} unless otherwise indicated.

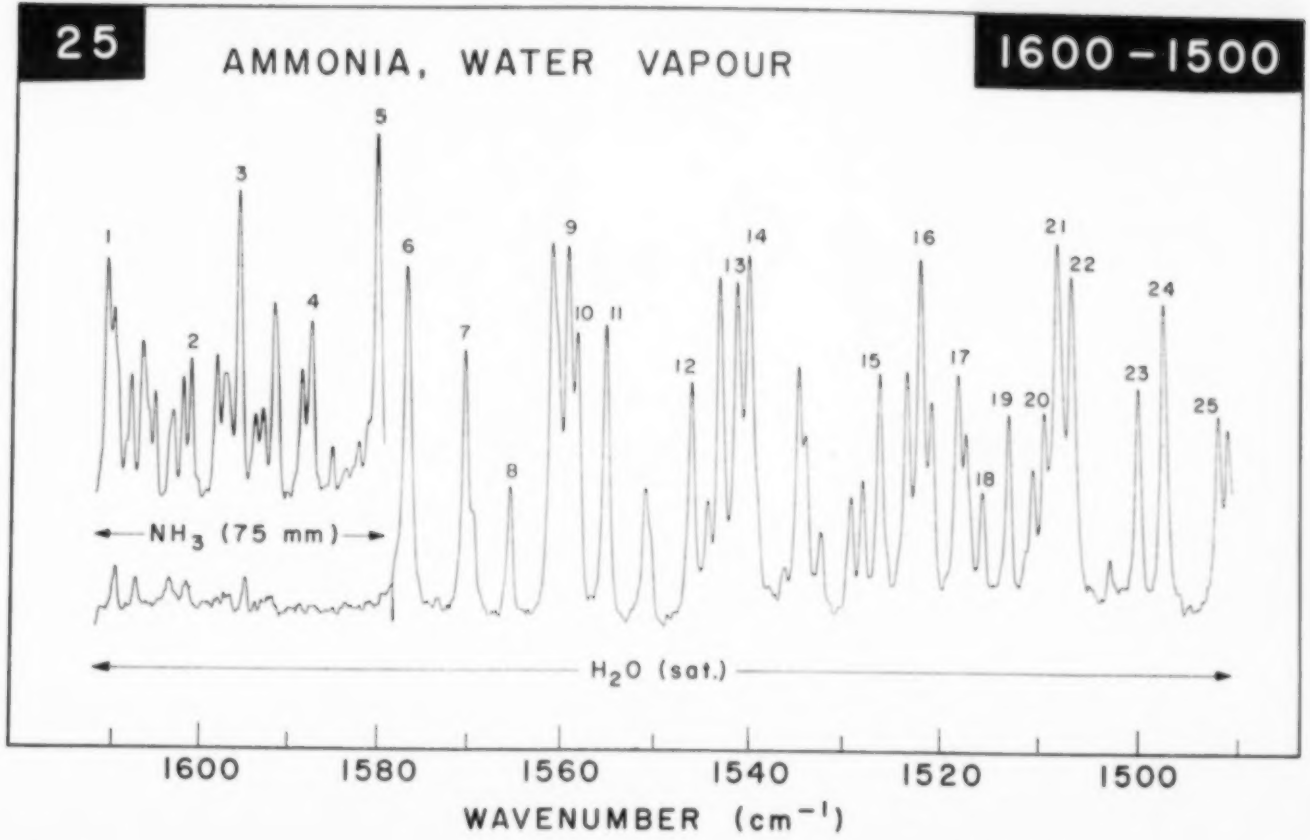
25
AMMONIA, WATER VAPOUR
1600 – 1500
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
NH3 (75 mm)
H2O (sat.)
1600
1580
1560
1540
1520
1500
WAVENUMBER (cm−1)

Chart 25. Ammonia (75 mm) and water vapour (saturated): 1600–1500 cm^{-1}

Ammonia (75 mm)		*Water vapour (saturated)*			
Line no.	*Wavenumber* (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	$1610{\cdot}3_5$ ($\pm 0{\cdot}2$ cm^{-1})	6	1576·2†‡	17	1517·5
2	1600·6 ($\pm 0{\cdot}2$ cm^{-1})	7	$1569{\cdot}8_5$	18	1515·0
3	$1594{\cdot}8_5$ ($\pm 0{\cdot}2$ cm^{-1})	8	$1564{\cdot}8_5$†‡	19	1512·3†
4	1586·9 ($\pm 0{\cdot}2$ cm^{-1})	9	$1558{\cdot}5_5$	20	1508·6
5	1579·5‡[b] ($\pm 0{\cdot}2$ cm^{-1})	10	$1557{\cdot}5_5$	21	1507·1
		11	1554·4‡	22	$1505{\cdot}6_5$
		12	$1545{\cdot}1_5$†	23	$1498{\cdot}8_5$†
		13	1540·3	24	$1496{\cdot}2_5$‡
		14	$1539{\cdot}0_5$	25	$1490{\cdot}8_5$
		15	1525·5		
		16	1521·4‡		

Resolution tests: Line no. 9–line no. 10: 1·0 cm^{-1}
Line no. 13–line no. 14: 1·25 cm^{-1}
Line no. 21–line no. 22: 1·45 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 25A*).
(a) The estimated uncertainty does not exceed $\pm 0{\cdot}1$ cm^{-1} unless otherwise indicated.
(b) Blend of two component lines.

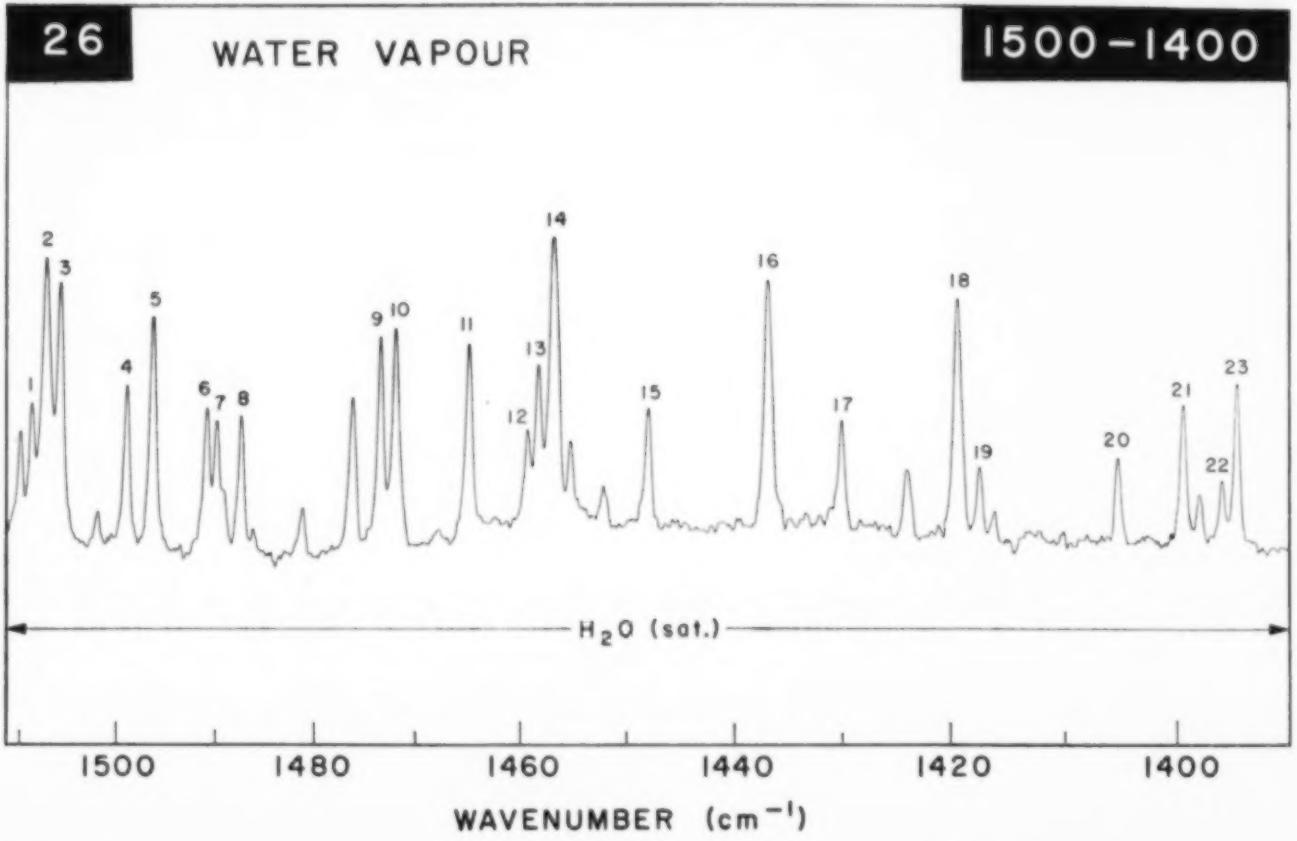
26
WATER VAPOUR
1500–1400
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
H2O (sat.)
1500
1480
1460
1440
1420
1400
WAVENUMBER (cm−1)

Chart 26. Water vapour (saturated): 1500–1400 cm^{-1}

Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	1508·6	13	$1458{\cdot}2_s$
2	1507·1	14	1456·8‡[b]
3	$1505{\cdot}6_s$	15	$1447{\cdot}9_s$†‡
4	1498·8†	16	1436·7‡
5	$1496{\cdot}2_s$‡	17	$1429{\cdot}9_s$†‡
6	$1490{\cdot}8_s$	18	1419·3‡
7	$1489{\cdot}8_s$	19	$1417{\cdot}4_s$†
8	1487·3†	20	1405·0†‡
9	1473·5	21	$1399{\cdot}1_s$‡
10	$1472{\cdot}0_s$	22	1395·8
11	1464·9†‡	23	$1394{\cdot}4_s$†
12	1459·3		

Resolution tests: Line no. 6–line no. 7: 1·0 cm^{-1}
Line no. 22–line no. 23: 1·35 cm^{-1}
Line no. 9–line no. 10: 1·45 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 26A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.
(b) Blend of two component lines.

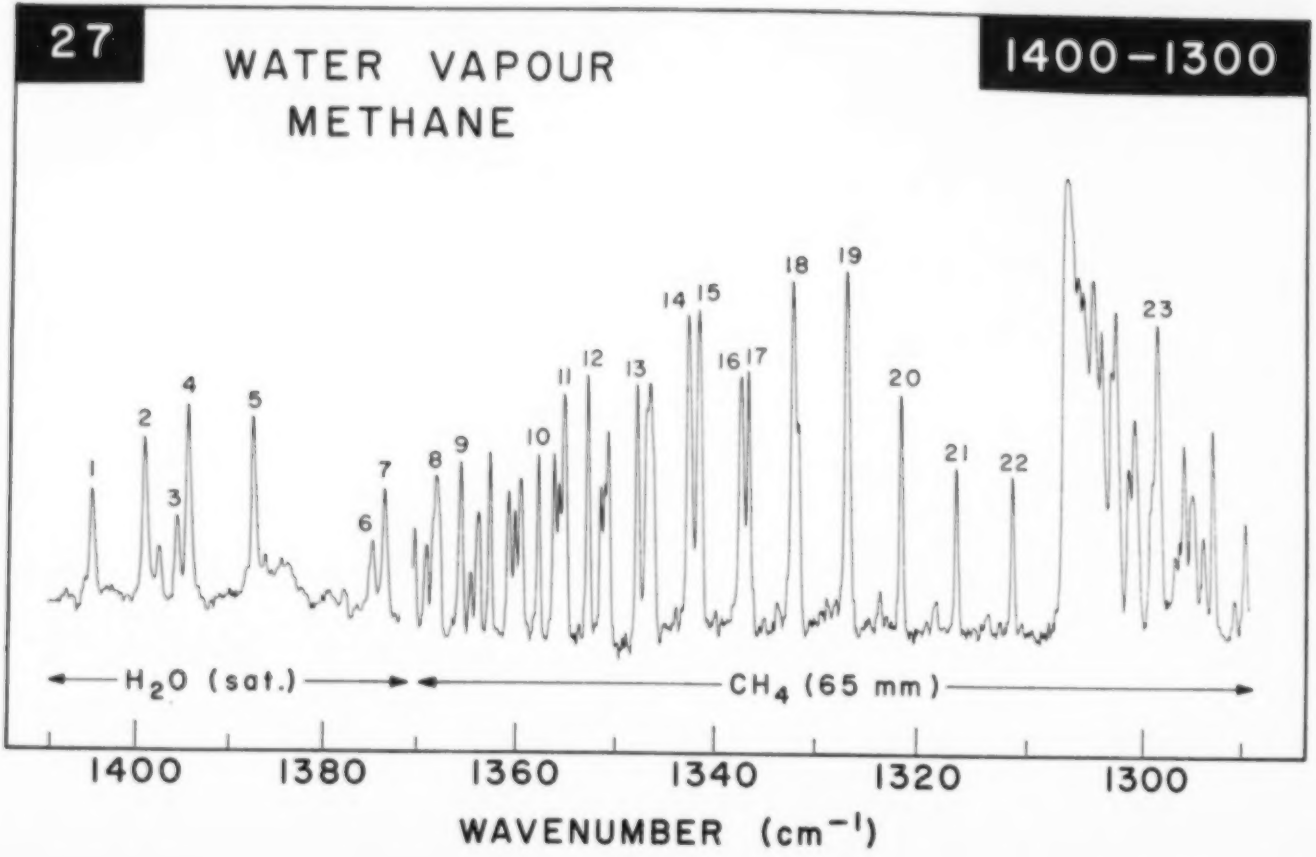
27
WATER VAPOUR
METHANE
1400–1300
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
H2O (sat.)
CH4 (65 mm)
1400
1380
1360
1340
1320
1300
WAVENUMBER (cm−1)

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Chart 27. Water vapour (saturated) and methane (60 mm): 1400–1300 cm^{-1}

Water vapour (saturated)		*Methane* (60 mm)			
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	1405·0†‡	8	$1368{\cdot}5_8$‡	16	$1337{\cdot}6_8$
2	$1399{\cdot}1_8$‡	9	$1366{\cdot}0_8$†	17	$1336{\cdot}8_8$
3	1395·8	10	1358·1	18	$1332{\cdot}4$†‡
4	$1394{\cdot}4_8$†	11	$1355{\cdot}5_8$	19	$1327{\cdot}2$†‡
5	$1387{\cdot}5_8$	12	$1353{\cdot}0_8$†	20	$1322{\cdot}1$†‡
6	1375·1†	13	1347·9	21	1316·8‡
7	$1373{\cdot}7_8$	14	1342·8	22	$1311{\cdot}4$†‡
		15	1341·8†	23	$1297{\cdot}6_8$†‡

Resolution tests: Line no. 16–line no. 17: 0·8 cm^{-1}
Line no. 14–line no. 15: 1·0 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 27A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

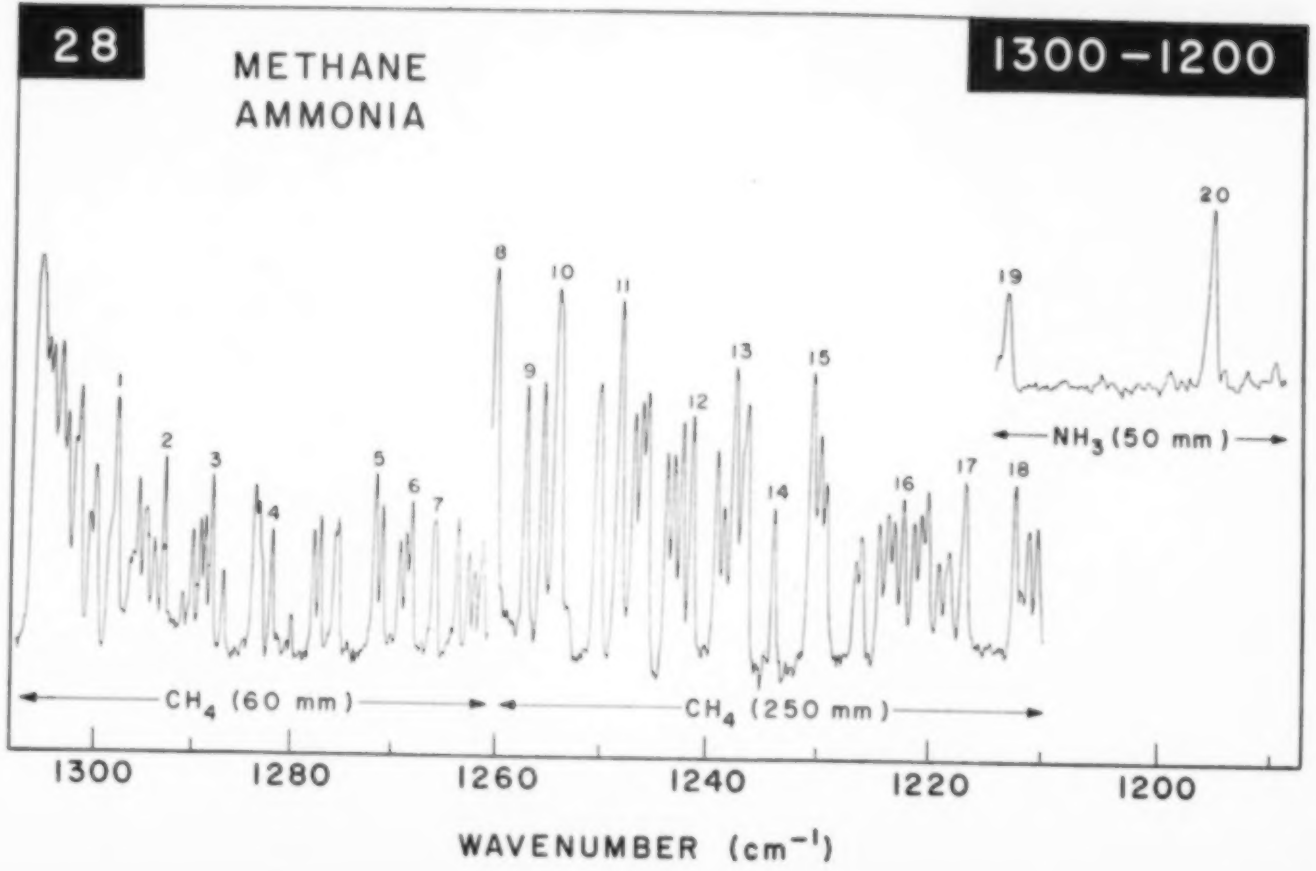
28
METHANE
AMMONIA
1300 – 1200
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
CH4 (60 mm)
CH4 (250 mm)
NH3 (50 mm)
1300
1280
1260
1240
1220
1200
WAVENUMBER (cm-1)

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Chart 28. Methane (65 mm), (250 mm) and ammonia (50 mm): 1300–1200 cm^{-1}

Methane (65 mm)		*Methane* (250 mm)		*Ammonia* (50 mm)	
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	$1297{\cdot}6_5$†‡	8	$1259{\cdot}7_5$	19	1212·7†‡
2	1292·6†	9	1256·6†	20	1195·0†‡
3	1287·8	10	$1253{\cdot}7_5$‡		
4	1281·6†	11	1247·8†		
5	1271·5	12	1241·0		
6	1267·9	13	1237·2‡		
7	1265·5†‡	14	$1233{\cdot}4_5$		
		15	1230·1		
		16	1221·9		
		17	$1216{\cdot}2_5$		
		18	1211·9		

† Part I calibration band.
‡ Suitable for use at lower resolution (*Chart 28A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

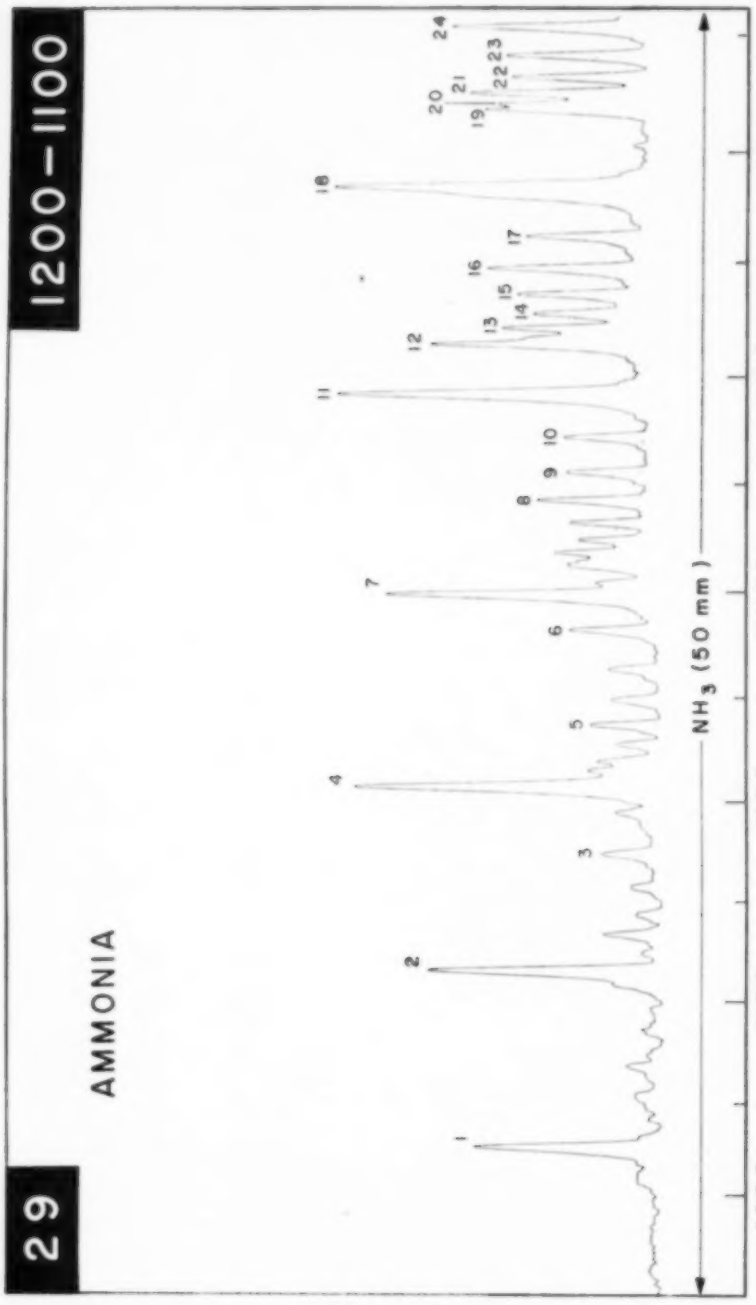
29
AMMONIA
1200–1100
NH_3 (50 mm)
1200
1180
1160
1140
1120
1100
WAVENUMBER (cm^{-1})

Chart 29. Ammonia (50 mm): 1200–1100 cm^{-1}

Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	1195·0†‡	13	$1116{\cdot}0_5$†
2	1177·1†‡	14	1114·7
3	1165·5	15	$1112{\cdot}9_5$
4	$1158{\cdot}9_5$†‡	16	1110·7†
5	$1152{\cdot}8_5$†	17	$1107{\cdot}8_5$
6	1143·9†	18	$1103{\cdot}4_5$†‡
7	$1140{\cdot}6_5$†‡	19	1096·7
8	$1131{\cdot}8_5$†	20	$1096{\cdot}1_5$
9	$1129{\cdot}2_5$	21	$1095{\cdot}1_5$†
10	$1126{\cdot}0_5$†	22	$1093{\cdot}7_5$
11	$1122{\cdot}1_5$†‡	23	$1091{\cdot}8_5$
12	$1117{\cdot}5_5$		

Resolution tests: Line no. 19–line no. 20: 0·55 cm^{-1}
Line no. 12–line no. 13: 1·5 cm^{-1}
Line no. 8–line no. 9: 2·6 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 29A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.

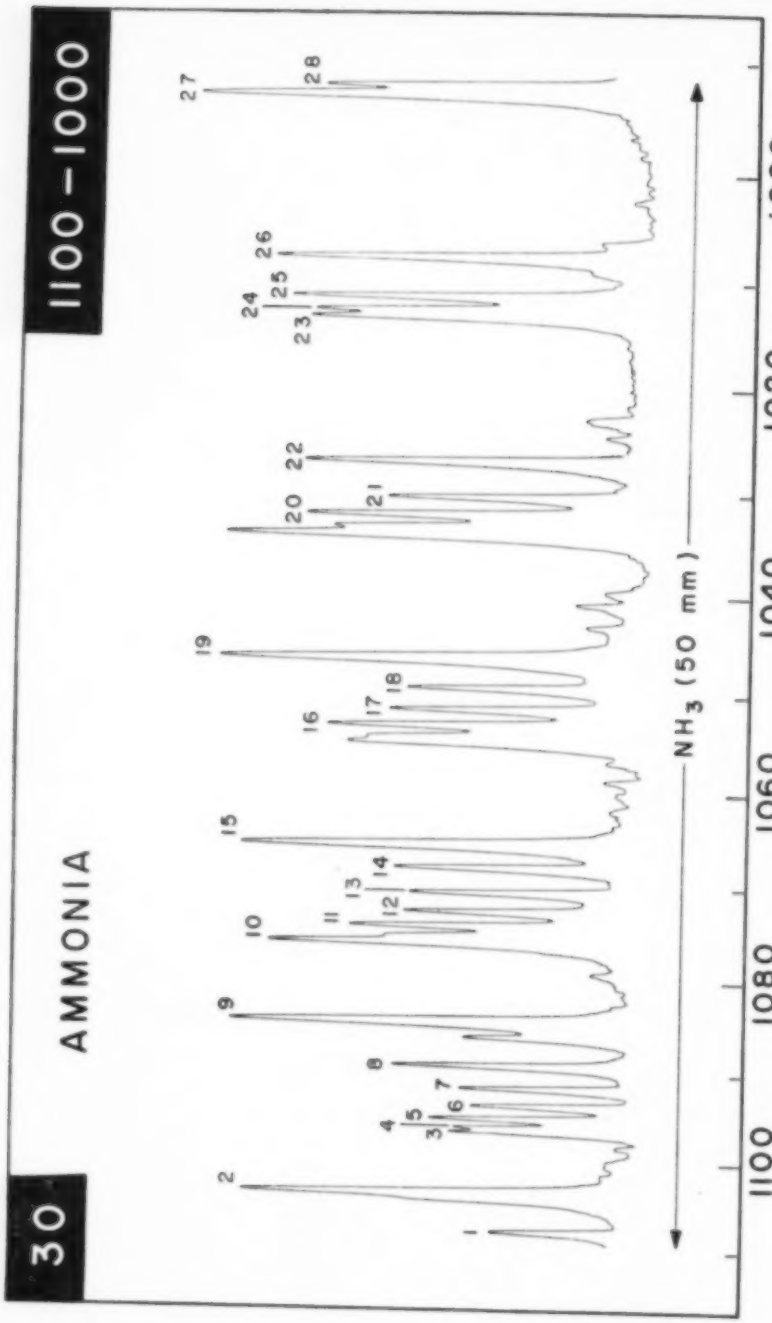
30
AMMONIA
1100 – 1000
NH_3 (50 mm)
WAVENUMBER (cm^{-1})
1100
1080
1060
1040
1020
1000
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28

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Chart 30. Ammonia (50 mm): 1100–1000 cm^{-1}

Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	$1107{\cdot}8_s$	15	$1065{\cdot}5_s$†‡
2	$1103{\cdot}4_s$†‡	16	$1053{\cdot}1_s$†
3	1096·7	17	1051·5
4	$1096{\cdot}1_s$	18	$1049{\cdot}3_s$
5	$1095{\cdot}1_s$†	19	$1046{\cdot}4$†‡
6	$1093{\cdot}7_s$	20	$1032{\cdot}1_s$†
7	$1091{\cdot}8_s$	21	1030·4
8	1089·4†	22	$1027{\cdot}0_s$†‡
9	1084·6†‡	23	1013·2
10	$1075{\cdot}9_s$[b]	24	$1012{\cdot}4_s$
11	$1074{\cdot}1_s$†	25	1011·2†
12	$1072{\cdot}6_s$	26	$1007{\cdot}5_s$†‡
13	1070·6†	27	992·6†[b]
14	1068·0	28	991·7†

Resolution tests: Line no. 3–line no. 4: 0·55 cm^{-1}
Line no. 23–line no. 24: 0·75 cm^{-1}
Line no. 10–line no. 11: 1·8 cm^{-1}

† Part I calibration band.
‡ Suitable for use under lower resolution (*Chart 30A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.
(b) Blend of two component lines.

31
AMMONIA
1000-900
NH3 (50 mm)
NH3 (15 mm)
NH3 (50 mm)
NH3 (15 mm)
NH3 (50 mm)
1000
980
960
940
920
900
WAVENUMBER (cm-1)

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Chart 31. Ammonia (50 mm) and (15 mm): 1000–900 cm^{-1}

Ammonia (50 mm)		*Ammonia* (15 mm)	
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	$1007{\cdot}5_5$ †‡	5	$967{\cdot}3_5$
2	$992{\cdot}6$ †[b]	6	$966{\cdot}8$
3	$991{\cdot}7$ †	7	$966{\cdot}2_5$
4	$971{\cdot}9$ †‡		
....	.....	....	.....
9	$959{\cdot}5$	17	$927{\cdot}3$
10	$957{\cdot}8_5$	18	$925{\cdot}6$
11	$951{\cdot}8$ †‡	19	$924{\cdot}0_5$
12	$949{\cdot}3_5$	20	$923{\cdot}6$
13	$948{\cdot}2_5$ †		
14	$937{\cdot}6$		
15	$935{\cdot}9$ †		
16	$934{\cdot}3$		
....	.....		
21	$921{\cdot}2_5$		
22	$918{\cdot}6$ †		
23	$915{\cdot}7$		
24	$912{\cdot}4$ ‡		
25	$908{\cdot}2$ †‡		
26	$892{\cdot}0_5$ †‡[b]		

Resolution tests: Line no. 19–line no. 20: 0·45 cm^{-1}
Line no. 5–line no. 6: 0·55 cm^{-1}
Line no. 2–line no. 3: 0·9 cm^{-1}
Line no. 12–line no. 13: 1·1 cm^{-1}

† Part I calibration band.
‡ Suitable for use under lower resolution (*Chart 31A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.
(b) Blend of two component lines.

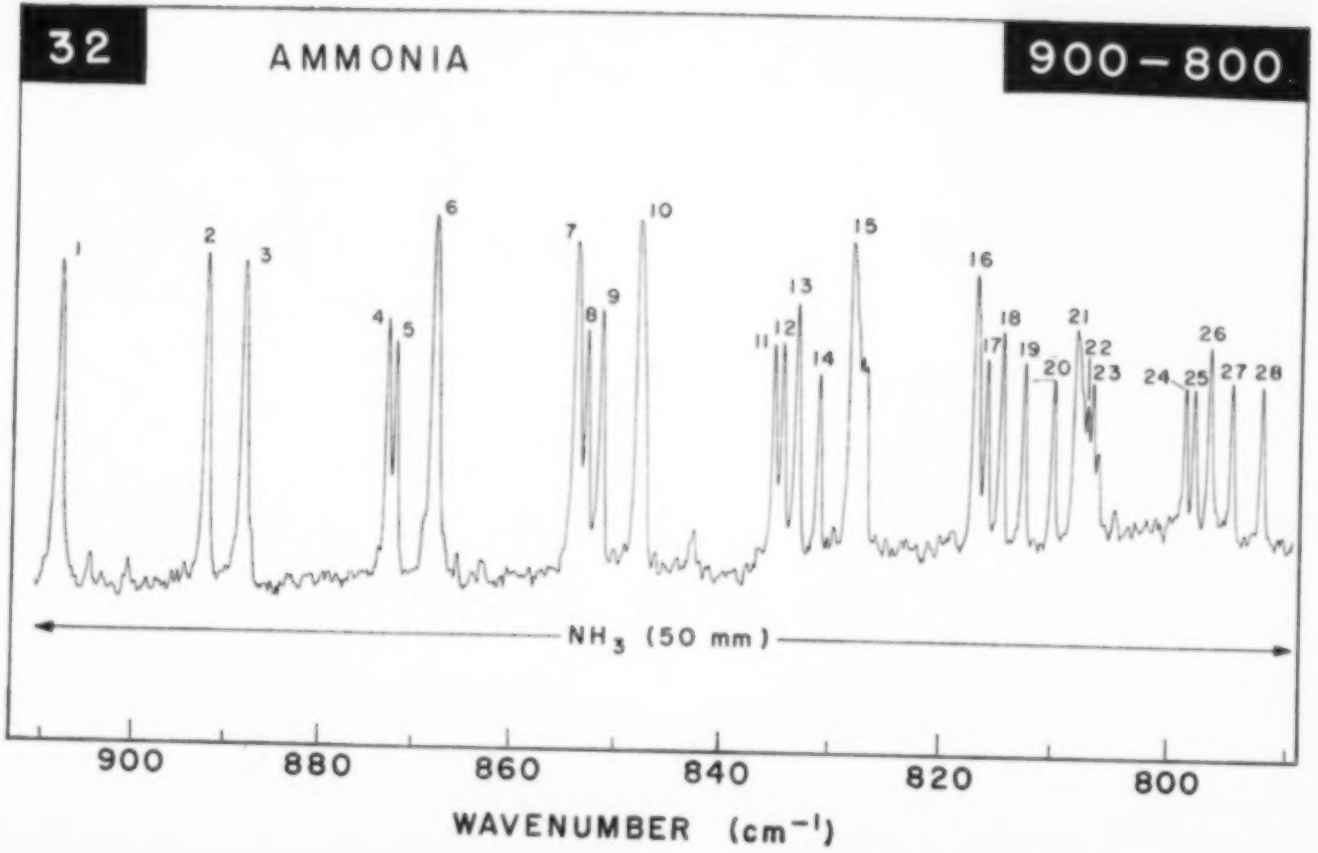
32
AMMONIA
900–800
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
NH3 (50 mm)
900
880
860
840
820
800
WAVENUMBER (cm⁻¹)

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Chart 32. Ammonia (50 mm): 900–800 cm^{-1}

Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	908·2†‡	16	$816·5_b$‡[b]
2	$892·0_b$†‡[b]	17	815·6
3	888·0†‡	18	$814·2_b$†
4	872·6†	19	812·3
5	$871·7_b$†	20	809·7†
6	867·8†‡[c]	21	807·5[c]
7	853·7	22	$806·7_b$
8	$852·7_b$	23	$806·2_b$
9	$851·3_b$†	24	$798·2_b$
10	847·7‡[b]	25	$797·4_b$
11	$834·8_b$†	26	$796·1_b$†
12	834·0	27	$794·2_b$
13	$832·6_b$	28	$791·7_b$†‡
14	830·7†		
15	$827·7_b$[b]		

Resolution tests: Line no. 22–line no. 23: 0·5 cm^{-1}
Line no. 4–line no. 5: 0·85 cm^{-1}
Line no. 16–line no. 17: 0·95 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 32A*).
(a) The estimated uncertainty does not exceed ±0·1 cm^{-1}.
(b) Blend of two component lines.
(c) Blend of three component lines.

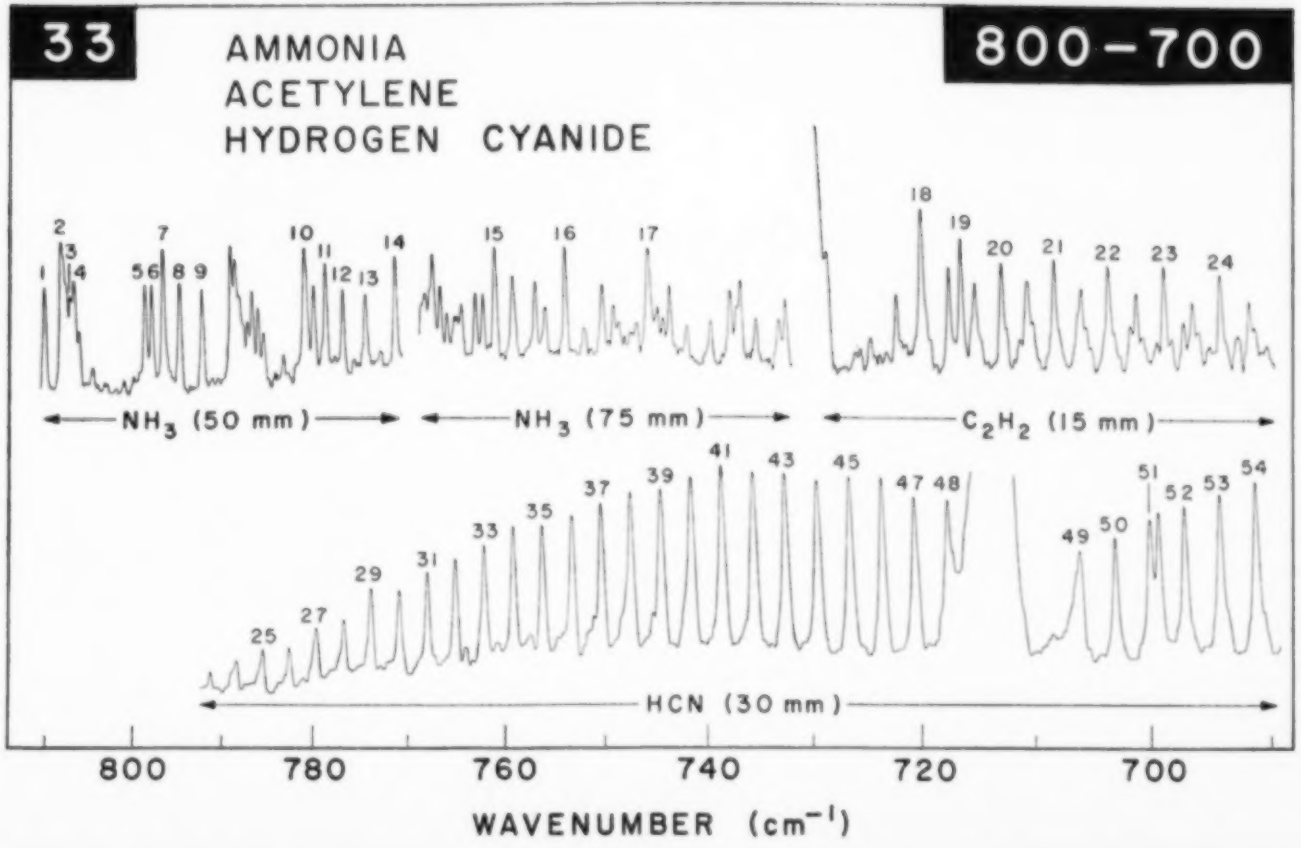
33
AMMONIA
ACETYLENE
HYDROGEN CYANIDE
800–700
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
27
29
31
33
35
37
39
41
43
45
47
48
49
50
51
52
53
54
NH3 (50 mm)
NH3 (75 mm)
C2H2 (15 mm)
HCN (30 mm)
800
780
760
740
720
700
WAVENUMBER (cm−1)

Chart 33. Ammonia (50 mm), (75 mm), acetylene (15 mm) and hydrogen cyanide (30 mm): 800–700 cm^{-1}

Ammonia (50 mm)		*Acetylene* (15 mm)		*Hydrogen cyanide* (30 mm)			
Line no.	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[a] (vac.) (cm^{-1})
1	809·7†	18	719·9‡	25	$785{\cdot}5_s$†‡	40	741·5†‡
2	807·5[c]	19	$716{\cdot}3_s$	26	$782{\cdot}6_s$†‡	41	$738{\cdot}5_s$†‡
3	$806{\cdot}7_s$	20	$712{\cdot}6_s$‡	27	$779{\cdot}7_s$†‡	42	735·6†‡
4	$806{\cdot}2_s$	21	$707{\cdot}9_s$‡	28	776·8†‡	43	$732{\cdot}6_s$†‡
5	$798{\cdot}2_s$	22	$703{\cdot}2_s$‡	29	$773{\cdot}8_s$†‡	44	729·7†‡
6	$797{\cdot}4_s$	23	698·5‡	30	$770{\cdot}9_s$†‡	45	$726{\cdot}7_s$†‡
7	$796{\cdot}1_s$†	24	693·8‡	31	768·0†‡	46	723·8†‡
8	$794{\cdot}2_s$			32	$765{\cdot}0_s$†‡	47	$720{\cdot}8_s$†‡
9	$791{\cdot}7_s$†‡			33	$762{\cdot}1_s$†‡	48	717·9†
10	780·4[b]			34	759·2†‡	49	$706{\cdot}0_s$†‡
11	778·3†‡			35	$756{\cdot}2_s$†‡	50	703·1†‡
12	776·5			36	$753{\cdot}3_s$†‡	51	$700{\cdot}1_s$†
13	774·0			37	$750{\cdot}3_s$†‡	52	697·2†‡
14	770·9†‡			38	747·4†‡	53	$694{\cdot}2_s$†‡
				39	$744{\cdot}4_s$†‡	54	691·3†‡
Ammonia (75 mm)							
15	760·7†‡						
16	753·6†						
17	745·4[c]						

Resolution tests: Line no. 3–line no. 4: 0·5 cm^{-1}
Line no. 29–line no. 30: 2·9 cm^{-1}
Line no. 53–line no. 54: 2·95 cm^{-1}

† Part 1 calibration band.
‡ Suitable for use under lower resolution (*Chart 33A*).
(a) The estimated uncertainty does not exceed $\pm 0{\cdot}1$ cm^{-1}.
(b) Blend of two component lines.
(c) Blend of three component lines.

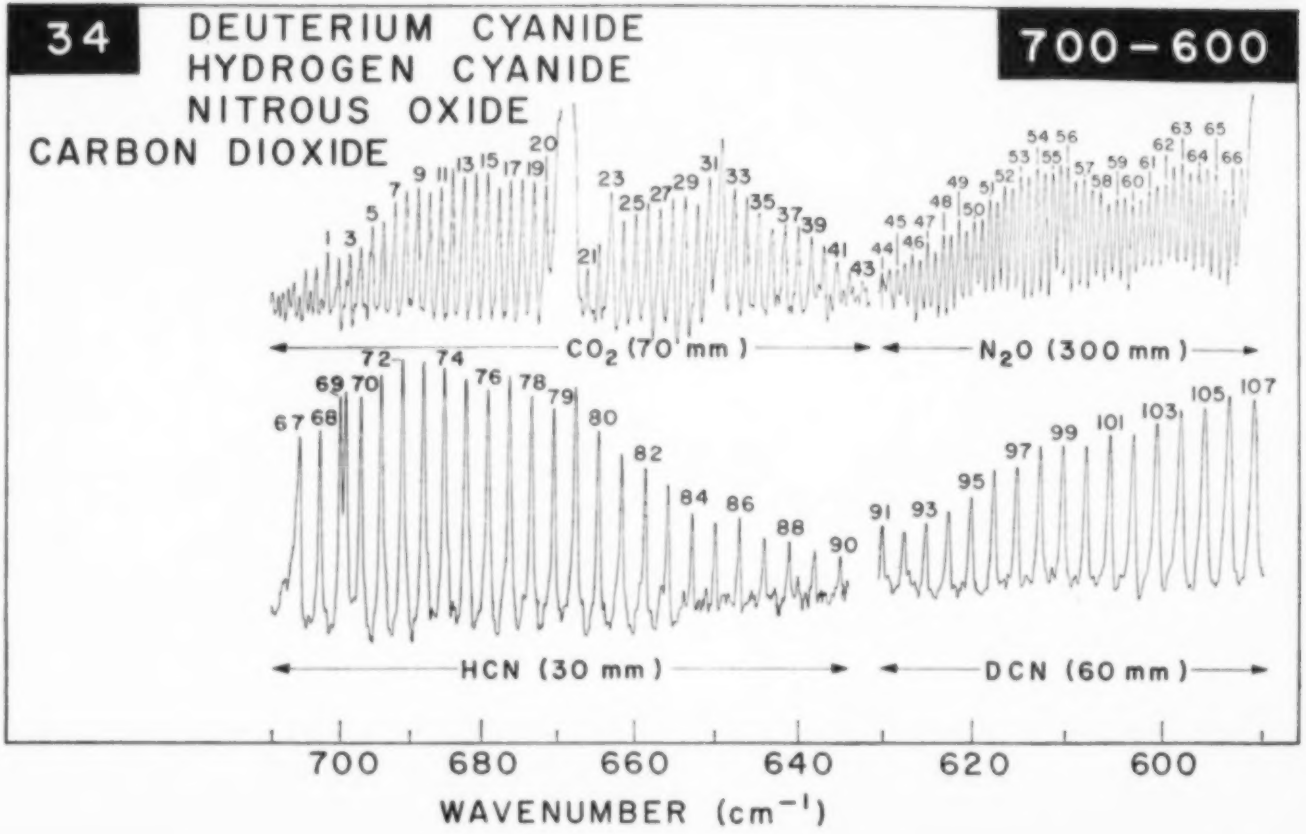
34
DEUTERIUM CYANIDE
HYDROGEN CYANIDE
NITROUS OXIDE
CARBON DIOXIDE
700-600
CO2 (70 mm)
N2O (300 mm)
HCN (30 mm)
DCN (60 mm)
700
680
660
640
620
600
WAVENUMBER (cm-1)

Chart 34. Carbon dioxide (70 mm), nitrous oxide (300 mm)[a], hydrogen cyanide (30 mm) and deuterium cyanide (60 mm): 700–600 cm^{-1}

Carbon dioxide (70 mm)				*Nitrous oxide* (300 mm)			
Line no.	*Wavenumber*[b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})
1	701·7†‡	24	$661{\cdot}1_5$†‡	44	$630{\cdot}1_5$	57	$608{\cdot}1_5$†
2	$700{\cdot}0_5$†‡	25	659·6†‡	45	$628{\cdot}4_5$†	58	$606{\cdot}4_5$†
3	$698{\cdot}4_5$†‡	26	$658{\cdot}0_5$†‡	46	$626{\cdot}7_5$†	59	$604{\cdot}7_5$†
4	696·8†‡	27	$656{\cdot}5_5$†‡	47	$625{\cdot}0_5$†	60	$603{\cdot}0_5$†
5	695·2†‡	28	655·0†‡	48	$623{\cdot}3_5$†	61	601·4†
6	693·6†‡	29	653·5†‡	49	621·7†	62	599·7†
7	692·0†‡	30	$651{\cdot}9_5$†‡	50	620·0†	63	$598{\cdot}0_5$†
8	$690{\cdot}3_5$†‡	31	650·4†‡	51	618·3†	64	$596{\cdot}3_5$†
9	688·8†‡	32	648·9†‡	52	616·6†	65	$594{\cdot}6_5$†
10	$687{\cdot}1_5$†‡	33	647·4†‡	53	614·9†	66	$592{\cdot}9_5$†
11	$685{\cdot}5_5$†‡	34	645·9†‡	54	613·2†		
12	$683{\cdot}9_5$†‡	35	$644{\cdot}3_5$†‡	55	611·5†		
13	682·4†‡	36	$642{\cdot}8_5$†‡	56	609·8†		
14	680·8†‡	37	$641{\cdot}3_5$†‡				
15	679·2†‡	38	$639{\cdot}8_5$†‡				
16	677·6†‡	39	$638{\cdot}3_5$†‡				
17	$676{\cdot}0_5$†‡	40	$636{\cdot}8_5$†‡				
18	$674{\cdot}4_5$†‡	41	635·4†				
19	672·9†‡	42	633·9†				
20	$671{\cdot}3_5$†‡	43	632·4†				
21	$665{\cdot}8_5$†						
22	664·3†						
23	662·7†‡						

(continued overleaf)

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Chart 34 (continued)

Hydrogen cyanide (30 mm)				*Deuterium cyanide* (60 mm)	
Line no.	*Wavenumber*[b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})	*Line no.*	*Wavenumber*[b] (vac.) (cm^{-1})
67	$706{\cdot}0_5$†‡	80[c]	664·7†‡	91	630·1
68	703·1†‡	81	$661{\cdot}7_5$†‡	92	$627{\cdot}6_5$
69	$700{\cdot}1_5$†	82	658·8†‡	93	625·2
70	697·2†‡	83	$655{\cdot}8_5$†‡	94	$622{\cdot}6_5$
71	$694{\cdot}2_5$†‡	84	652·9†‡	95	$620{\cdot}3_5$‡
72	691·3†‡	85	649·9†	96	617·8‡
73	$688{\cdot}3_5$†‡	86	647·0†	97	$615{\cdot}3_5$‡
74	$685{\cdot}3_5$†‡	87	$644{\cdot}0_5$†	98	$612{\cdot}8_5$‡
75	682·4†‡	88	641·1†	99	$610{\cdot}4_5$‡
76	$679{\cdot}4_5$†‡	89	$638{\cdot}1_5$†	100	608·0‡
77	676·5†‡	90	635·2	101	$605{\cdot}5_5$‡
78	$673{\cdot}5_5$†‡			102	603·1‡
79[c]	670·6†			103	600·6‡
				104	$598{\cdot}2_5$‡
				105	595·8‡
				106	593·3‡
				107	590·9‡

Resolution tests: The individual band spacing in the nitrous oxide spectrum is approx. 0·85 cm^{-1}
Line no. 13–line no. 14: 1·6 cm^{-1}
Line no. 99–line no. 100: 2·45 cm^{-1}
Line no. 74–line no. 75: 2·95 cm^{-1}

† Part I calibration line.
‡ Suitable for use under lower resolution (*Chart 34A*).
(a) Note that alternate lines are omitted.
(b) The estimated uncertainty does not exceed ±0·1 cm^{-1}.
(c) Note that the line following no. 79 is omitted; it is superimposed on the *Q*-branch of carbon dioxide.

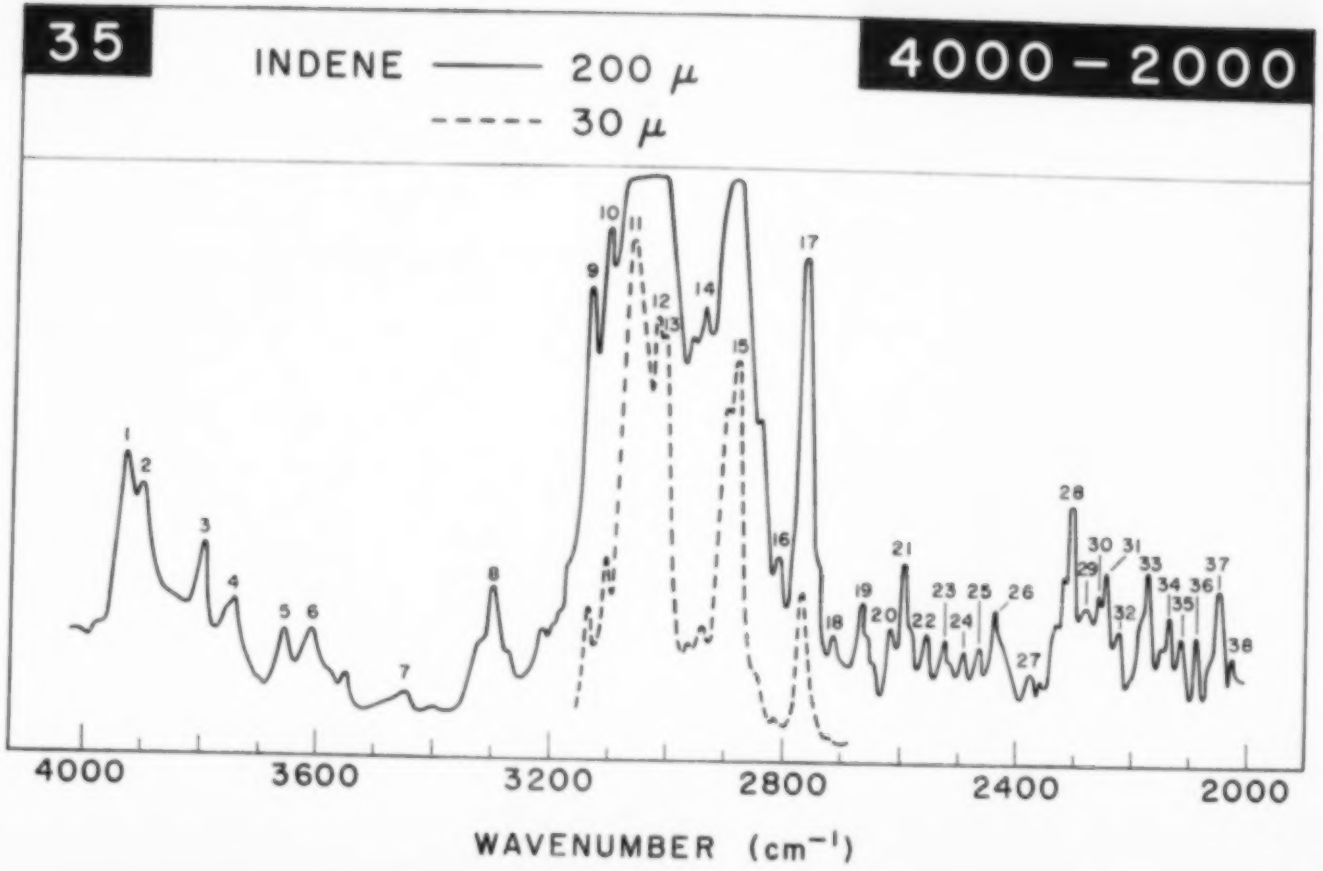
35
INDENE —— 200 μ
----- 30 μ
4000 – 2000
4000
3600
3200
2800
2400
2000
WAVENUMBER (cm⁻¹)

Chart 35. Indene (liquid film)[a]: 4000–2000 cm^{-1}

Band no.	*Wavenumber* (vac.) (cm^{-1})	*Band no.*	*Wavenumber* (vac.) (cm^{-1})	*Band no.*	*Wavenumber* (vac.) (cm^{-1})
1	3926·5 ± 1	13	3015·0 ± 0·5*	25	2465·6 ± 0·5* §
2	3900·7 ± 0·5*	14	2943·8 ± 1*	26	2439·5 ± 1 §
3	3797·5 ± 1	15	2887·0 ± 1	27	2379·0 ± 1* §
4	3747·5 ± 2* §	16	2812·5 ± 1*	28	2304·8 ± 0·5
5	3656·7 ± 1 §	17	2771·0 ± 0·5	29	2271·5 ± 0·5* §
6	3610·0 ± 2 §	18	2718·0 ± 1* §	30	2258·0 ± 0·5* §
7	3455·0 ± 3 §	19	2673·7 ± 1	31	2243·7 ± 0·5 §
8	3297·0 ± 1·5	20	2622·3 ± 0·5*	32	2223·0 ± 2* §
9	3139·5 ± 1*	21	2598·6 ± 0·5	33	2172·8 ± 0·5
10	3110·0 ± 1*	22	2558·5 ± 1 §	34	2135·8 ± 0·5
11	3068·5 ± 2·5 §	23	2525·9 ± 0·5	35	2113·5 ± 0·5
12	3025·6 ± 0·5*	24	2490·3 ± 0·5* §	36	2090·2 ± 0·5
				37	2049·6 ± 0·5
				38	2027·4 ± 0·5* §

§ Because of asymmetry, superposition on atmospheric water vapour or carbon dioxide lines, or for other reasons, these bands are less satisfactory; they are included to provide secondary calibration points in regions where better bands are not available.
* These bands may not be resolved by smaller prism spectrometers.
(a) The indene should be sealed in glass ampoules immediately after distillation and used only from freshly opened ampoules.

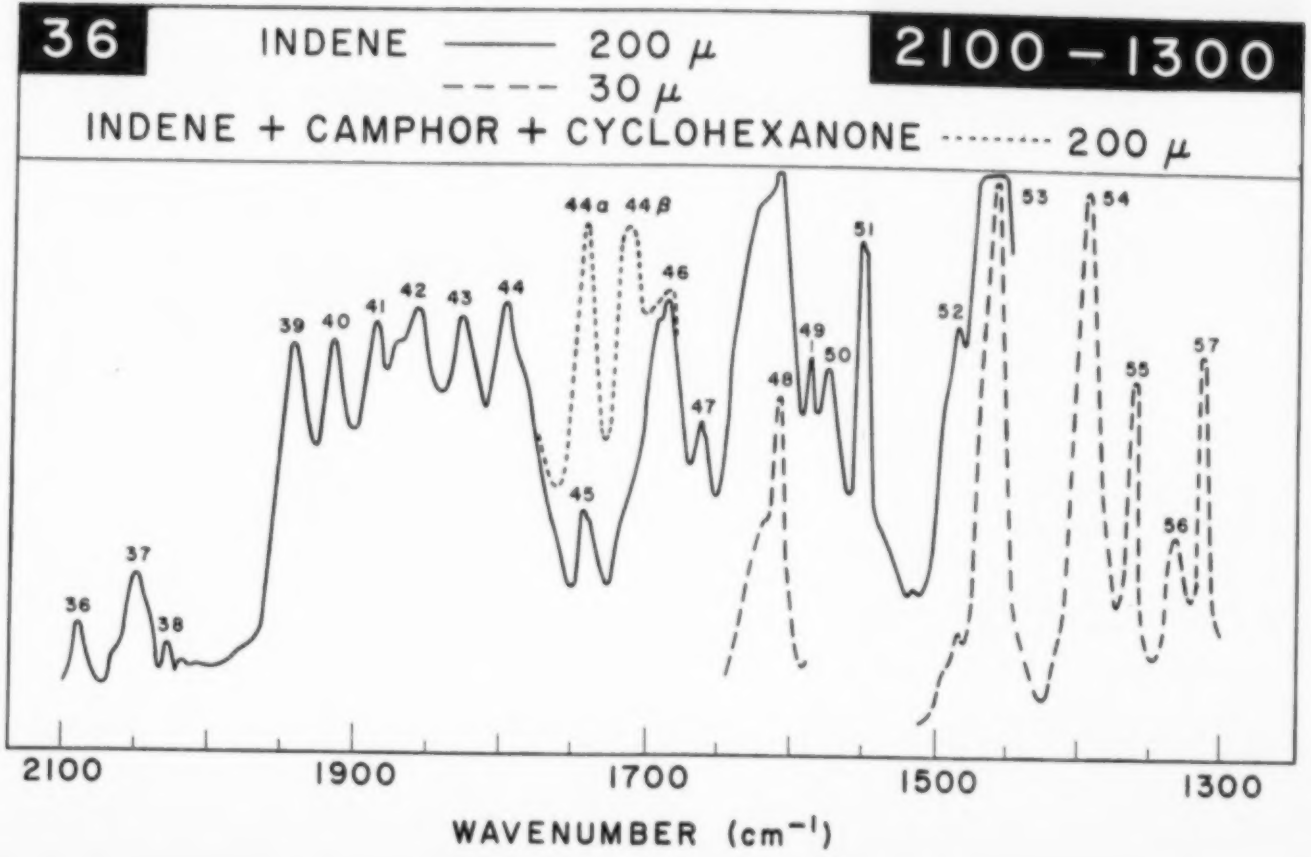
36
INDENE —— 200 μ
---- 30 μ
2100 – 1300
INDENE + CAMPHOR + CYCLOHEXANONE ····· 200 μ
36
37
38
39
40
41
42
43
44
44α
44β
45
46
47
48
49
50
51
52
53
54
55
56
57
2100
1900
1700
1500
1300
WAVENUMBER (cm⁻¹)

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Chart 36. Indene (liquid film)[a]: 2100–1300 cm^{-1}

Band no.	*Wavenumber* (vac.) (cm^{-1})	*Band no.*	*Wavenumber* (vac.) (cm^{-1})
36	2090·2 ± 0·5	47	1661·5 ± 0·5 §
37	2049·6 ± 0·5	48	1609·6 ± 0·2
38	2027·4 ± 0·5* §	49	1587·7 ± 0·2
39	1943·2 ± 0·5	50	1574·3 ± 0·5 §
40	1915·0 ± 0·3	51	1553·3 ± 0·5 §
41	1884·5 ± 0·5	52	1483·2 ± 0·5* §
42	1856·7 ± 0·3	53	1457·8 ± 0·5
43	1825·5 ± 0·5	54	1393·2 ± 1 §
44	1796·9 ± 0·3	55	1361·3 ± 0·4
44α	1741·8 ± 0·5 (camphor)[b]	56	1332·5 ± 0·5 §
44β	1713·5 ± 1 (cyclohexanone)[b]	57	1312·5 ± 0·3
45	1738·2 ± 1 §		
46	1686·0 ± 2 §		

§, *, (a) See footnotes to *Chart 35*.

(b) To overcome a lack of suitable calibration points in the indene spectrum between bands no. 44 and 47 it is suggested that 0·8 weight per cent of camphor and cyclohexanone be added. These additives introduce the additional bands no. 44α and 44β. They do not significantly displace any of the indene bands outside the region 1780–1690 cm^{-1} nor do they introduce any extra bands in other regions of the spectrum. They have no deleterious effect on the chemical stability of indene.

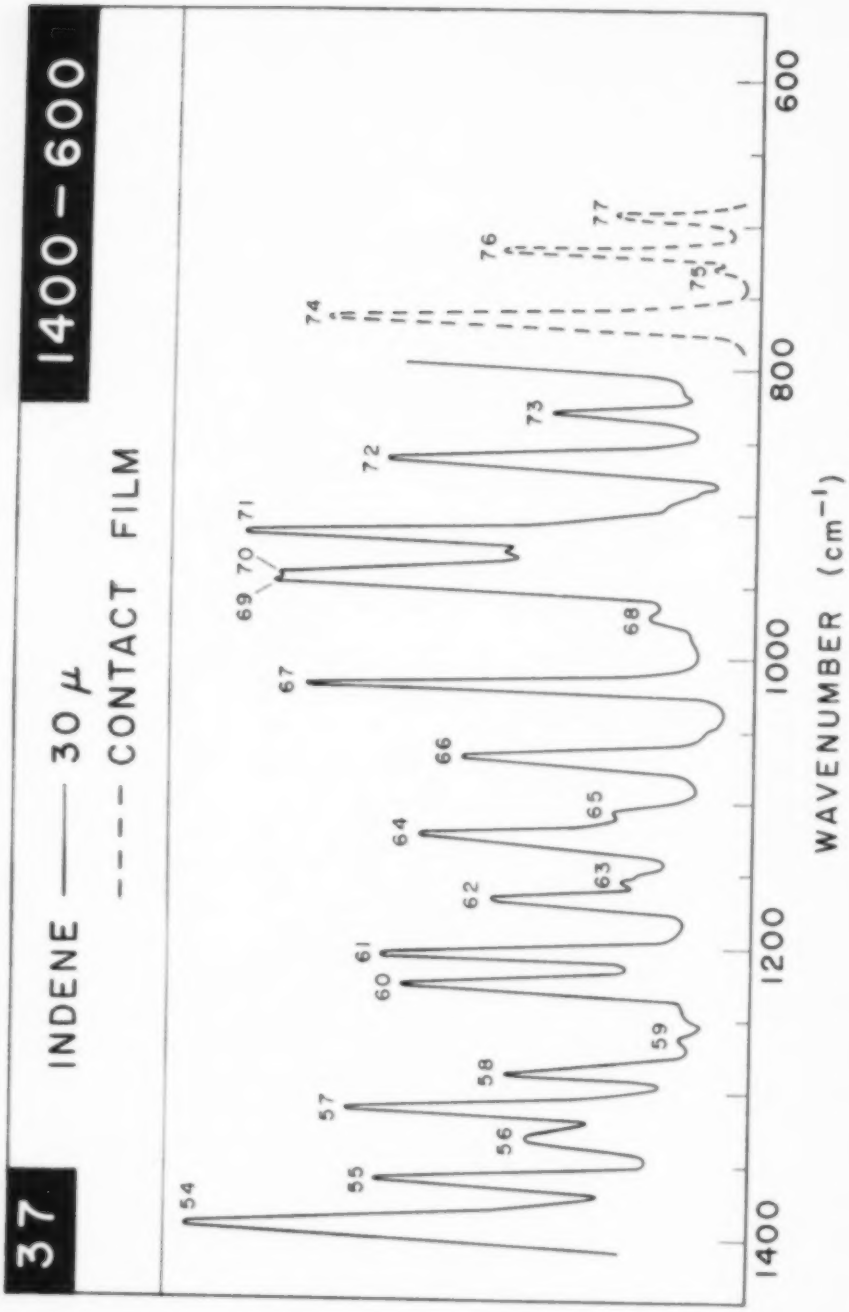
37
INDENE —— 30 μ
---- CONTACT FILM
1400-600
1400
1200
1000
800
600
WAVENUMBER (cm⁻¹)
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77

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Chart 37. Indene (liquid film)[(a)]; 1400–600 cm^{-1}

Band no.	*Wavenumber* (vac.) (cm^{-1})	*Band no.*	*Wavenumber* (vac.) (cm^{-1})
54	1393·2 ± 1§	66	1067·9 ± 0·2
55	1361·3 ± 0·4	67	1018·6 ± 0·2
56	1332·5 ± 0·5§	68	972·0 ± 0·5*§
57	1312·5 ± 0·3	69	947·2 ± 0·3§
58	1287·8 ± 0·2	70	942·3 ± 0·3*§
59	1263·8 ± 0·5*§	71	914·8 ± 0·2
60	1226·2 ± 0·2	72	861·3 ± 0·2
61	1205·2 ± 0·2	73	830·5 ± 0·2
62	1166·2 ± 0·3	74	765·4 ± 0·5
63	1154·5 ± 0·5*§	75	730·1 ± 0·2
64	1122·7 ± 0·2§	76	718·2 ± 0·3
65	1106·4 ± 0·5*§	77	692·8 ± 0·7§

§, *; (a) See footnotes to *Chart 35*.

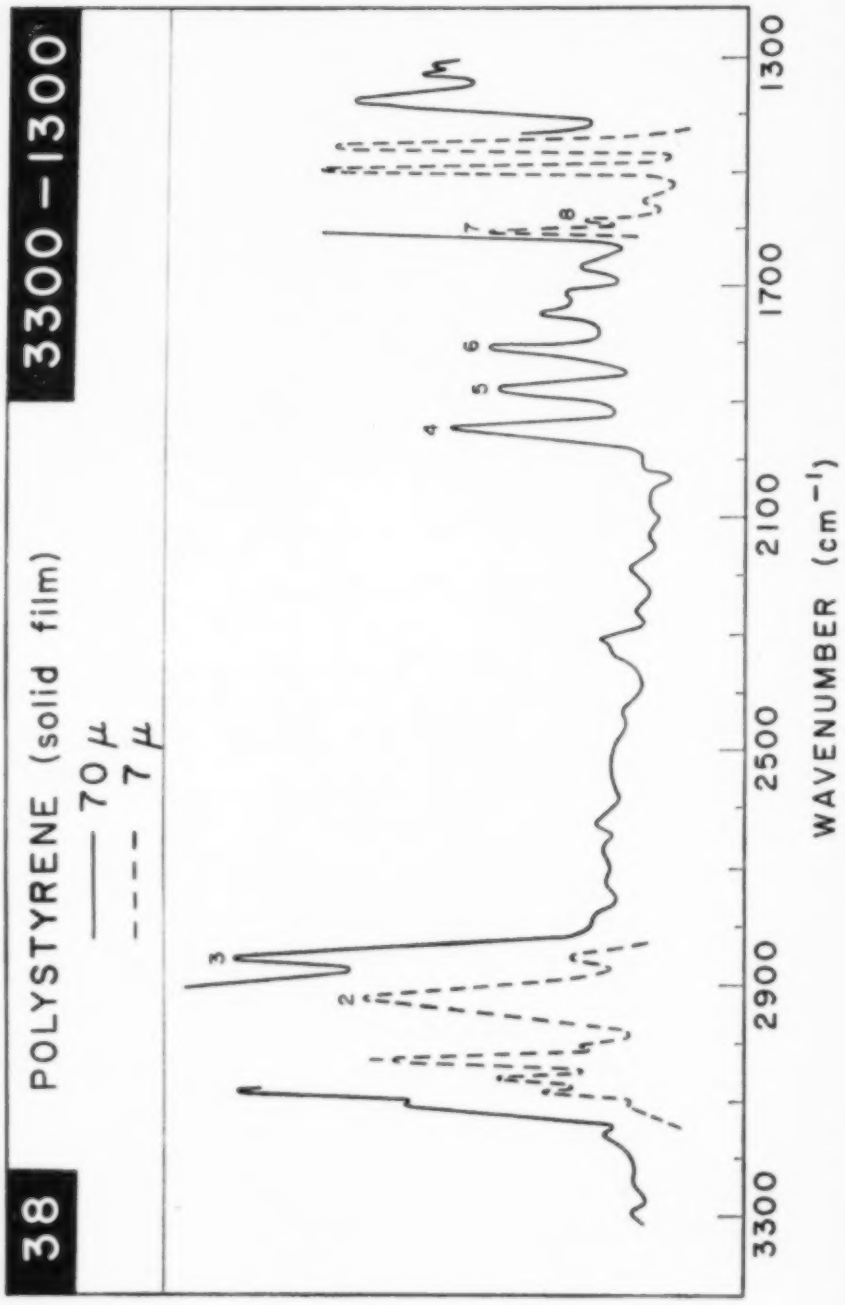
38
POLYSTYRENE (solid film)
70 μ
7 μ
3300-1300
3300
2900
2500
2100
1700
1300
WAVENUMBER (cm⁻¹)

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Chart 38. Polystyrene (solid film)[a]: 3300–1300 cm^{-1}

Band no.	*Wavenumber* (vac.) (cm^{-1})
1	3027·1 ± 0·3
2	2924 ± 2
3	2850·7 ± 0·3
4	1944·0 ± 1
5	1871·0 ± 0·3
6	1801·6 ± 0·3
7	1601·4 ± 0·3
8	1583·1 ± 0·3

(a) Films from commercial sources of polystyrene frequently exhibit strong interference patterns; such films should be slightly bent or otherwise deformed before using for calibration purposes.

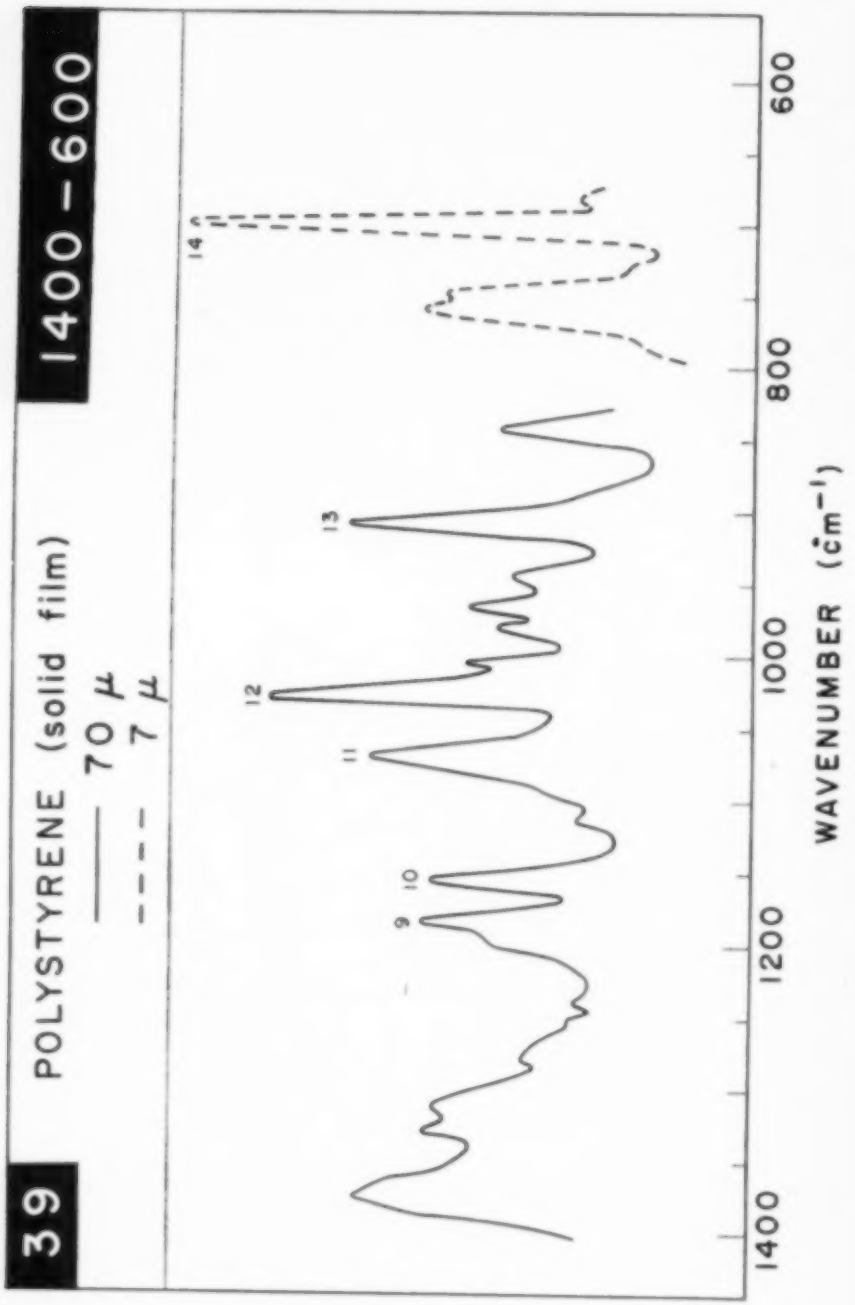
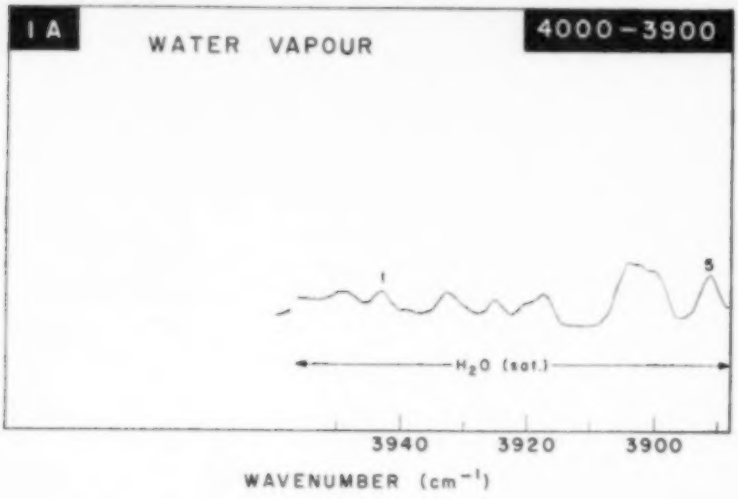
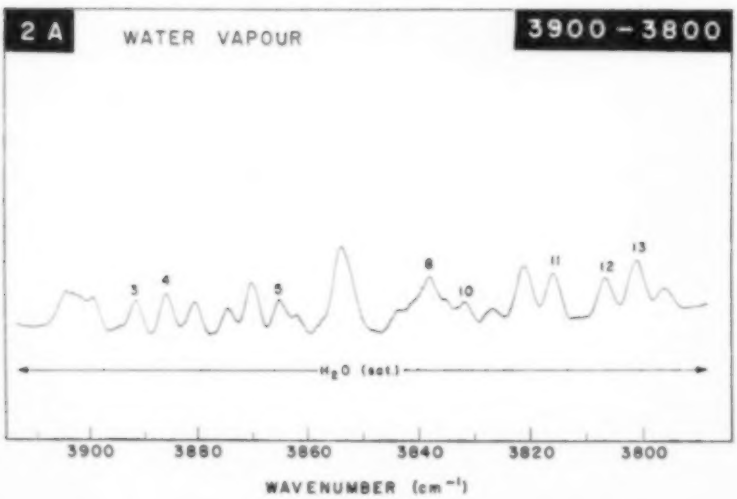

39
POLYSTYRENE (solid film)
70 μ
7 μ
1400 – 600
9
10
11
12
13
14
1400
1200
1000
800
600
WAVENUMBER (cm⁻¹)

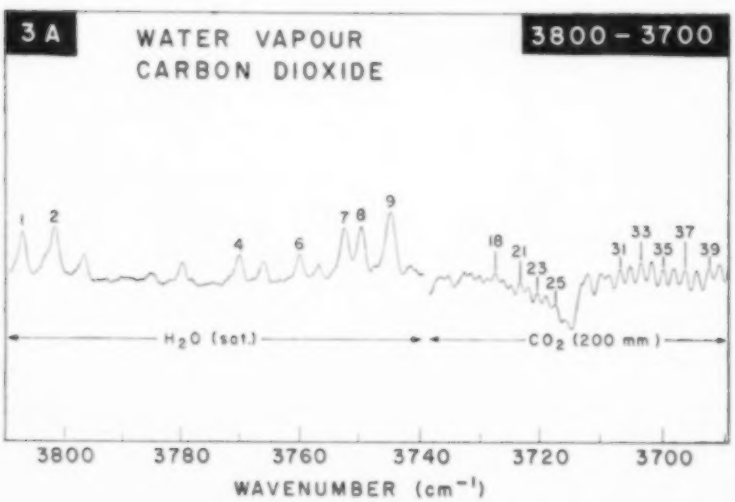
Chart 39. Polystyrene (solid film)[a]: 1400–600 cm^{-1}

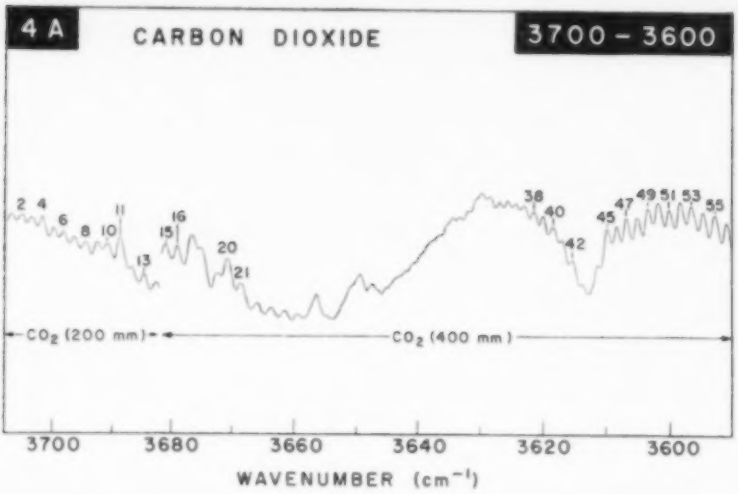
Band no.	*Wavenumber* (vac.) (cm^{-1})
9	1181·4 ± 0·3
10	1154·3 ± 0·3
11	1069·1 ± 0·3
12	1028·0 ± 0·3
13	906·7 ± 0·3
14	698·9 ± 0·5

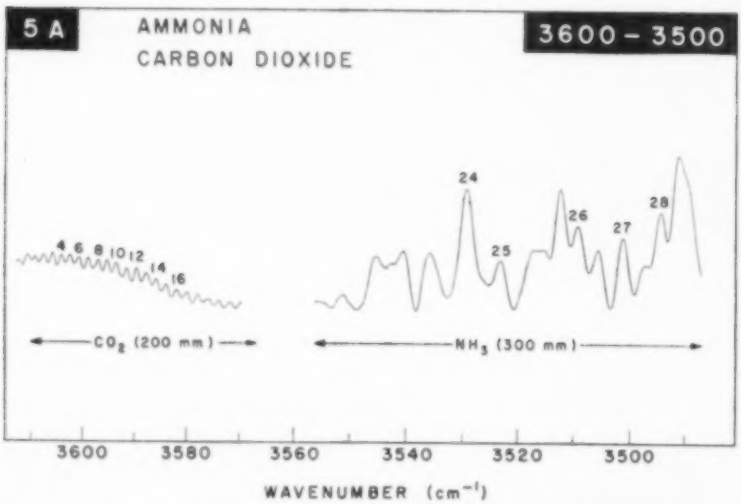
(a) See footnote to *Chart 38*.

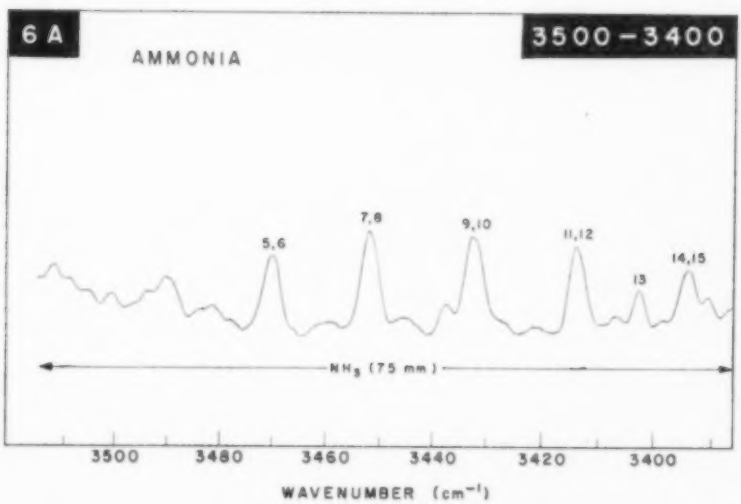

1 A
WATER VAPOUR
4000 – 3900
1
5
H_2O (sat.)
3940
3920
3900
WAVENUMBER (cm^{-1})

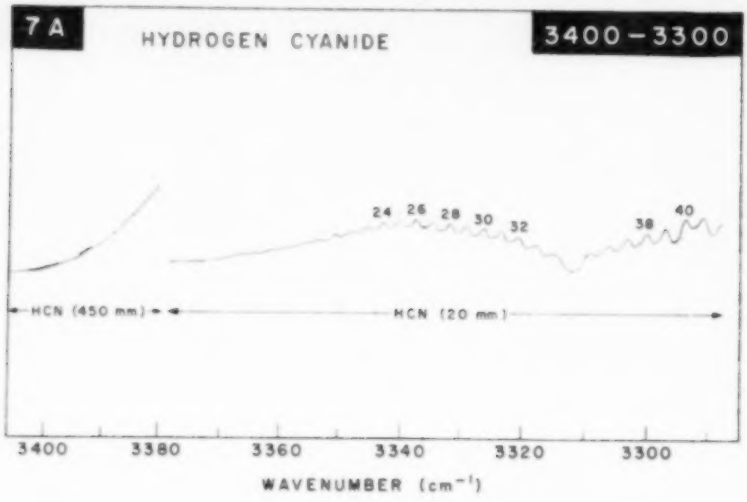

2 A
WATER VAPOUR
3900 – 3800
3
4
5
8
10
11
12
13
H_2O (sat.)
3900
3880
3860
3840
3820
3800
WAVENUMBER (cm^{-1})

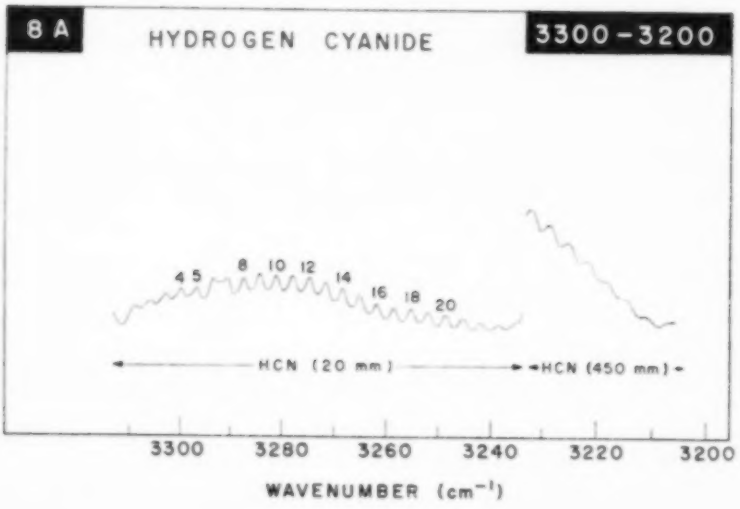

3 A
WATER VAPOUR
CARBON DIOXIDE
3800 – 3700
1
2
4
6
7
8
9
18
21
23
25
31
33
35
37
39
H_2O (sat.)
CO_2 (200 mm)
3800
3780
3760
3740
3720
3700
WAVENUMBER (cm^{-1})

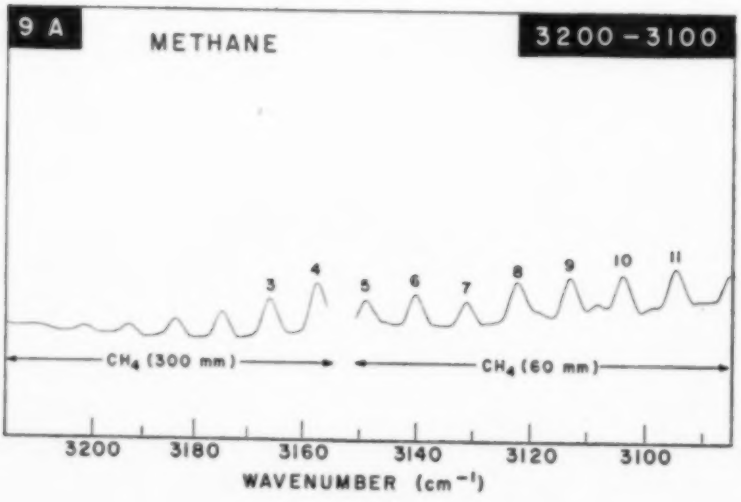

4 A
CARBON DIOXIDE
3700 – 3600
2 4 6 8 10 11 13 15 16 20 21 38 40 42 45 47 49 51 53 55
CO_2 (200 mm)
CO_2 (400 mm)
3700 3680 3660 3640 3620 3600
WAVENUMBER (cm^{-1})

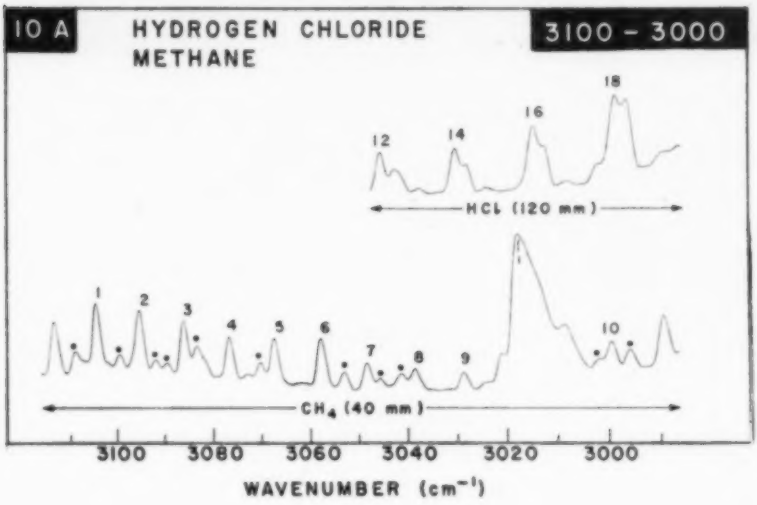

5 A
AMMONIA
CARBON DIOXIDE
3600 – 3500
4 6 8 10 12 14 16 24 25 26 27 28
CO_2 (200 mm)
NH_3 (300 mm)
3600 3580 3560 3540 3520 3500
WAVENUMBER (cm^{-1})

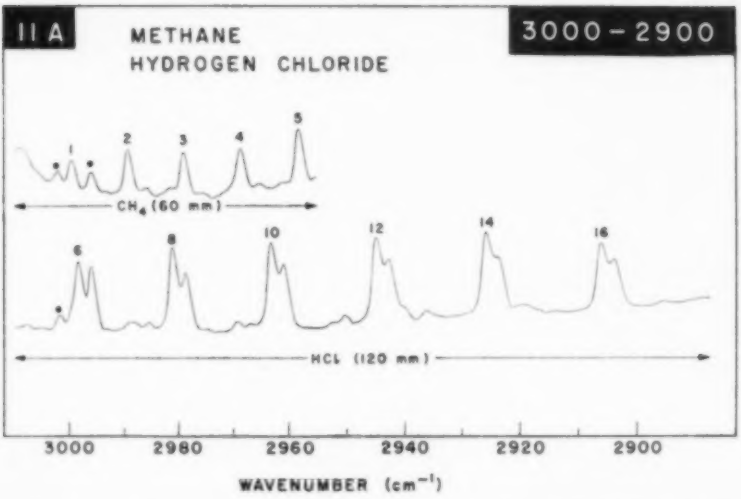

6 A
AMMONIA
3500 – 3400
5,6 7,8 9,10 11,12 13 14,15
NH_3 (75 mm)
3500 3480 3460 3440 3420 3400
WAVENUMBER (cm^{-1})

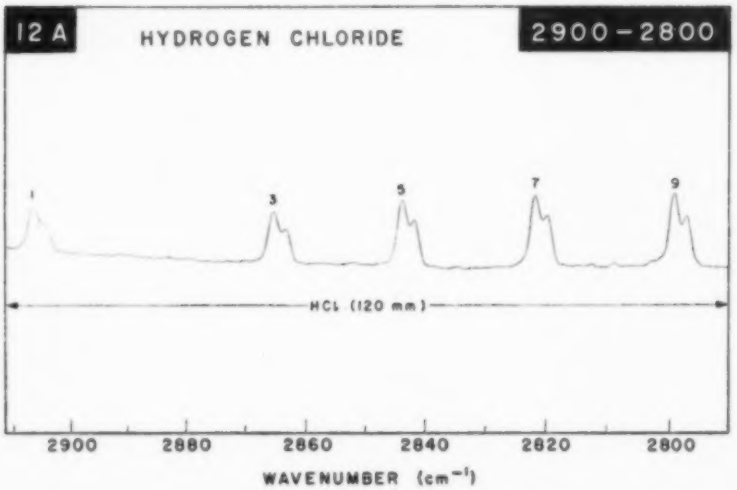

7 A
HYDROGEN CYANIDE
3400 – 3300
24 26 28 30 32 38 40
HCN (450 mm)
HCN (20 mm)
3400 3380 3360 3340 3320 3300
WAVENUMBER (cm⁻¹)

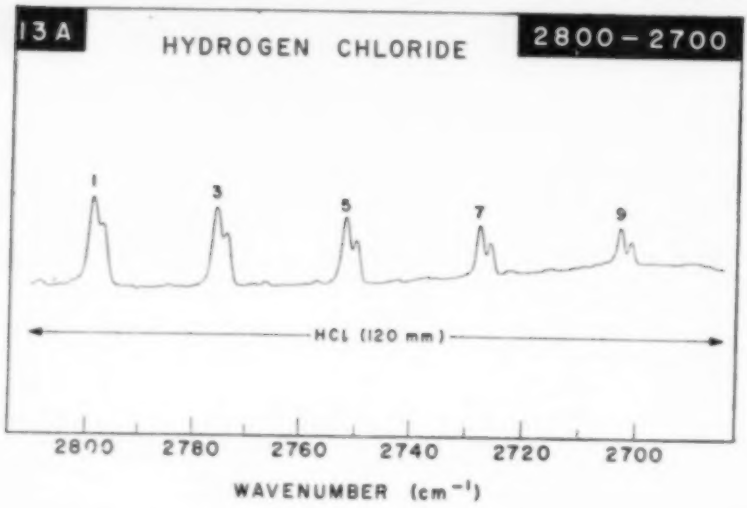

8 A
HYDROGEN CYANIDE
3300 – 3200
4 5 8 10 12 14 16 18 20
HCN (20 mm)
HCN (450 mm)
3300 3280 3260 3240 3220 3200
WAVENUMBER (cm⁻¹)

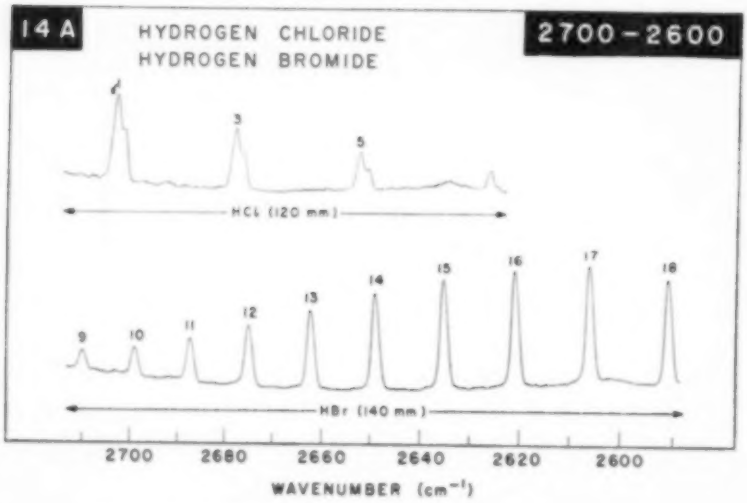

9 A
METHANE
3200 – 3100
3 4 5 6 7 8 9 10 11
CH4 (300 mm)
CH4 (60 mm)
3200 3180 3160 3140 3120 3100
WAVENUMBER (cm⁻¹)

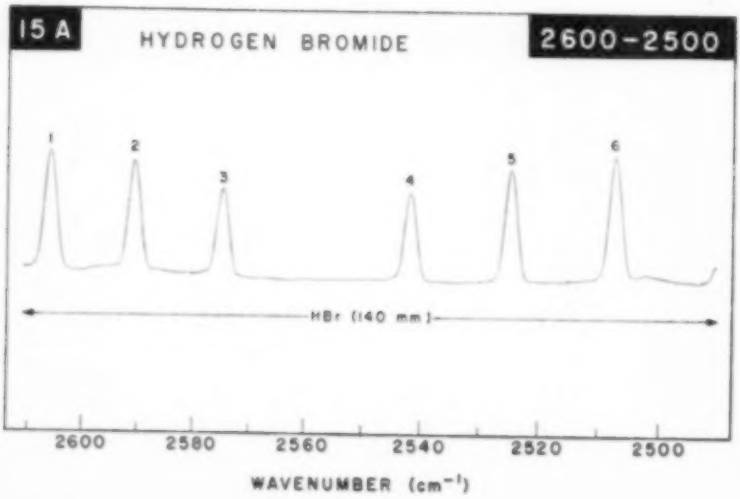

10 A
HYDROGEN CHLORIDE
METHANE
3100 - 3000
12
14
16
18
HCl (120 mm)
1
2
3
4
5
6
7
8
9
10
CH4 (40 mm)
3100
3080
3060
3040
3020
3000
WAVENUMBER (cm-1)

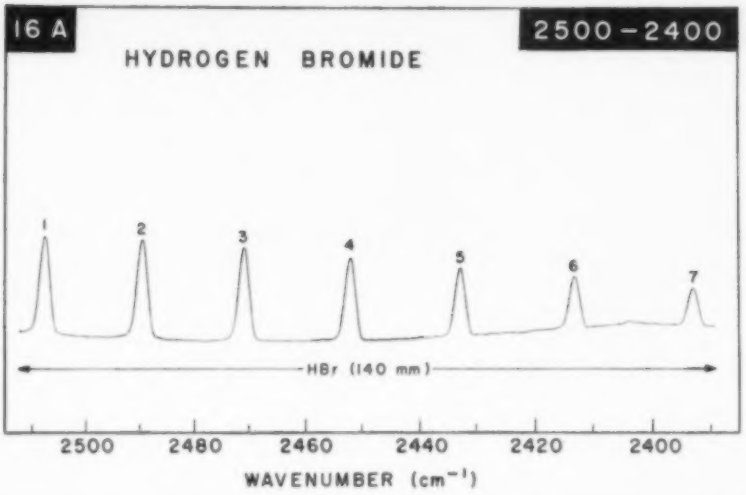

11 A
METHANE
HYDROGEN CHLORIDE
3000 - 2900
1
2
3
4
5
CH4 (60 mm)
6
8
10
12
14
16
HCl (120 mm)
3000
2980
2960
2940
2920
2900
WAVENUMBER (cm-1)

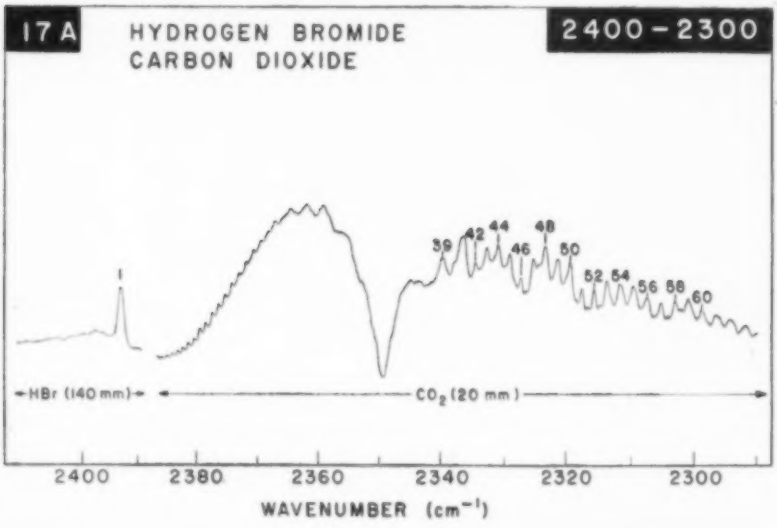

12 A
HYDROGEN CHLORIDE
2900 - 2800
1
3
5
7
9
HCl (120 mm)
2900
2880
2860
2840
2820
2800
WAVENUMBER (cm-1)

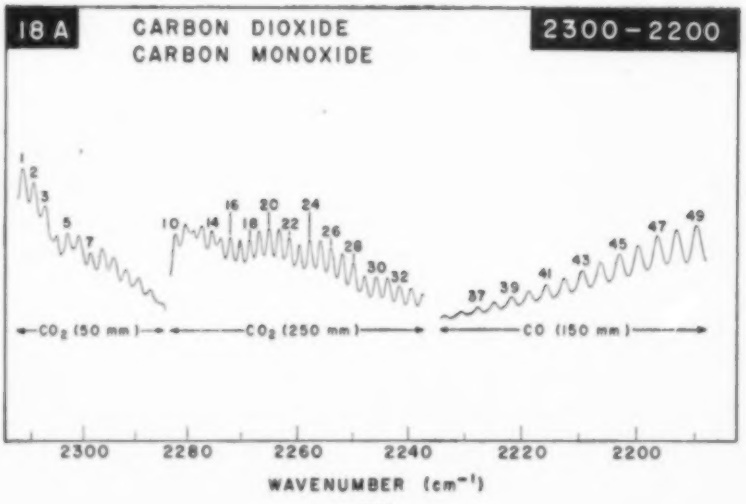

13 A
HYDROGEN CHLORIDE
2800 – 2700
1
3
5
7
9
HCl (120 mm)
2800
2780
2760
2740
2720
2700
WAVENUMBER (cm⁻¹)

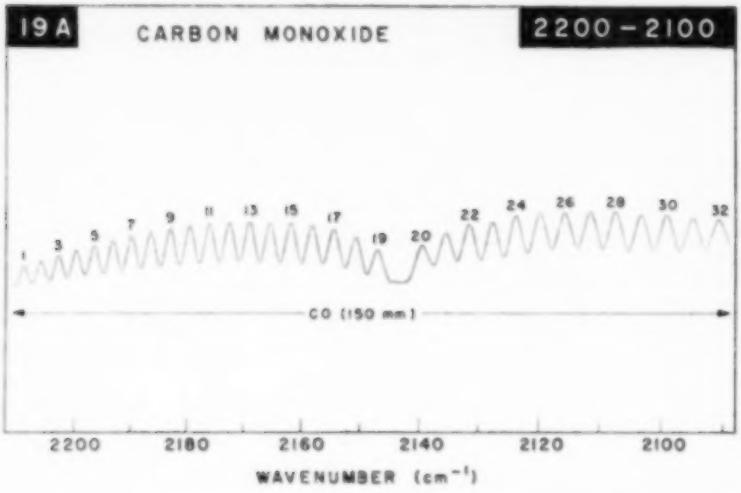

14 A
HYDROGEN CHLORIDE
HYDROGEN BROMIDE
2700 – 2600
1
3
5
HCl (120 mm)
9
10
11
12
13
14
15
16
17
18
HBr (140 mm)
2700
2680
2660
2640
2620
2600
WAVENUMBER (cm⁻¹)

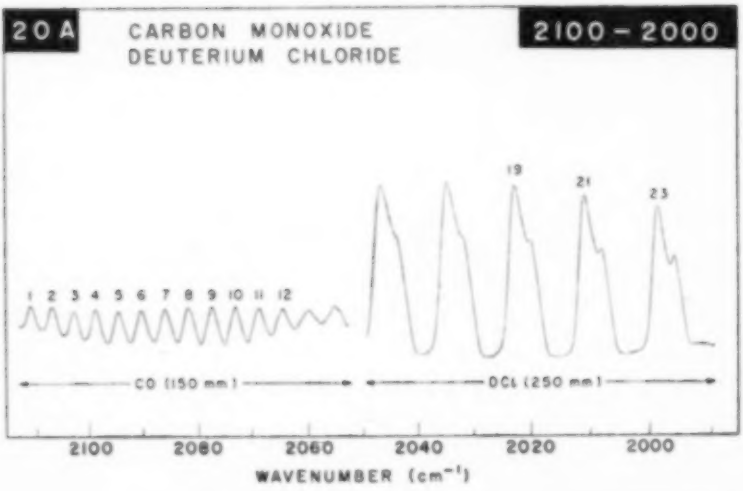

15 A
HYDROGEN BROMIDE
2600 – 2500
1
2
3
4
5
6
HBr (140 mm)
2600
2580
2560
2540
2520
2500
WAVENUMBER (cm⁻¹)

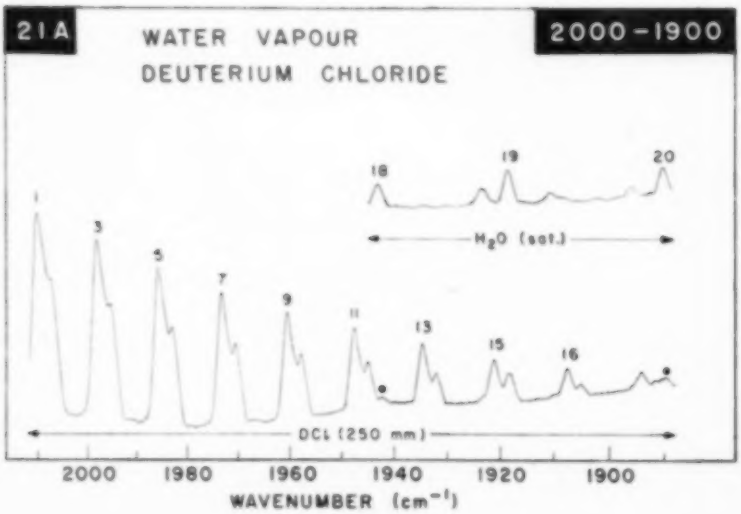

16 A
2500 – 2400
HYDROGEN BROMIDE
1
2
3
4
5
6
7
HBr (140 mm)
2500
2480
2460
2440
2420
2400
WAVENUMBER (cm⁻¹)

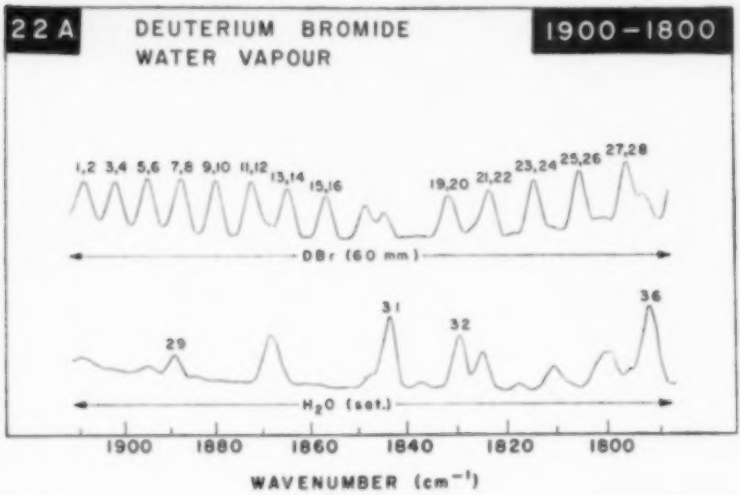

17 A
HYDROGEN BROMIDE
CARBON DIOXIDE
2400 – 2300
1
39
42
44
46
48
50
52
54
56
58
60
HBr (140 mm)
CO₂ (20 mm)
2400
2380
2360
2340
2320
2300
WAVENUMBER (cm⁻¹)

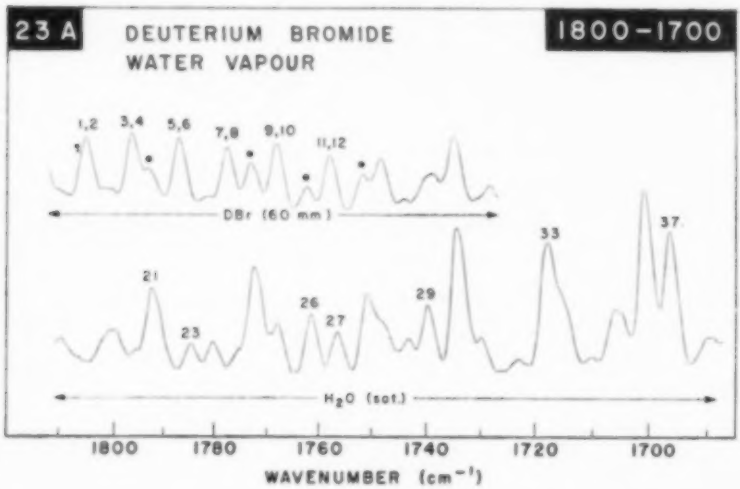

18 A
CARBON DIOXIDE
CARBON MONOXIDE
2300 – 2200
1
2
3
5
7
10
14
16
18
20
22
24
26
28
30
32
37
39
41
43
45
47
49
CO₂ (50 mm)
CO₂ (250 mm)
CO (150 mm)
2300
2280
2260
2240
2220
2200
WAVENUMBER (cm⁻¹)

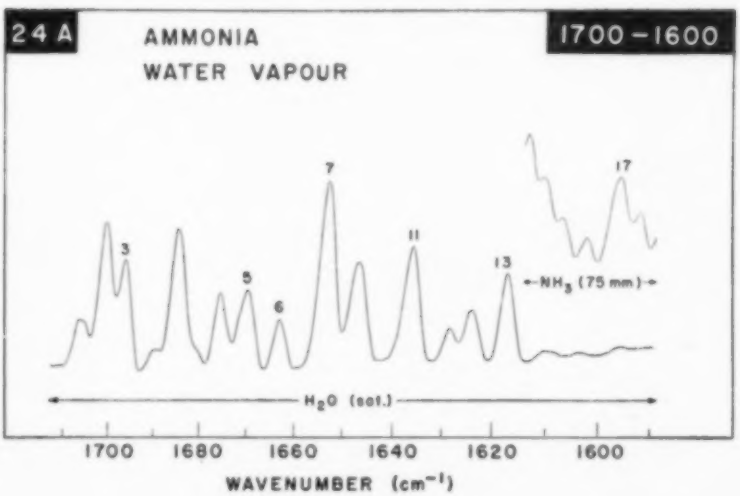

19A
CARBON MONOXIDE
2200 – 2100
1 3 5 7 9 11 13 15 17 19 20 22 24 26 28 30 32
CO (150 mm)
2200 2180 2160 2140 2120 2100
WAVENUMBER (cm⁻¹)

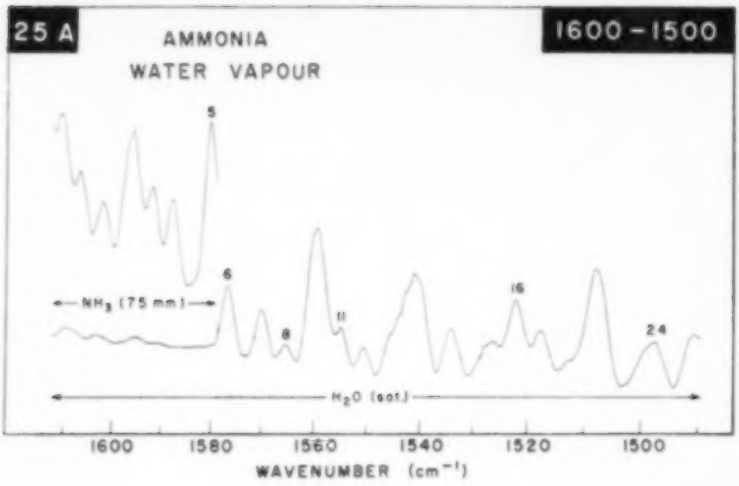

20A
CARBON MONOXIDE
DEUTERIUM CHLORIDE
2100 – 2000
1 2 3 4 5 6 7 8 9 10 11 12
19 21 23
CO (150 mm)
DCl (250 mm)
2100 2080 2060 2040 2020 2000
WAVENUMBER (cm⁻¹)

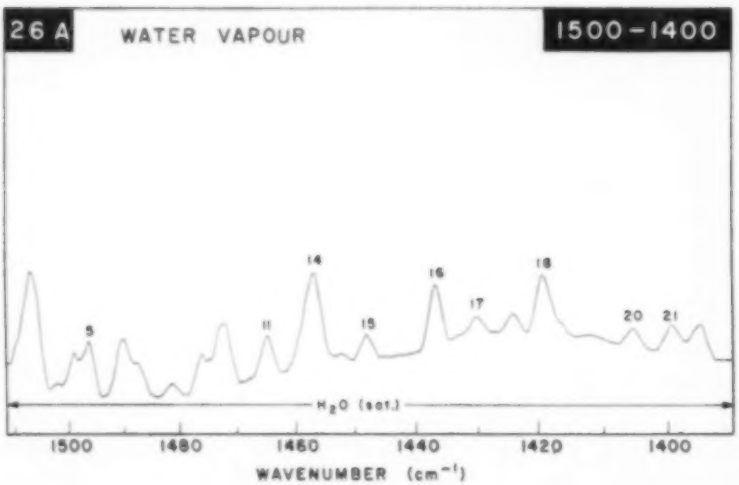

21A
WATER VAPOUR
DEUTERIUM CHLORIDE
2000 – 1900
18 19 20
H₂O (sat.)
1 3 5 7 9 11 13 15 16
DCl (250 mm)
2000 1980 1960 1940 1920 1900
WAVENUMBER (cm⁻¹)

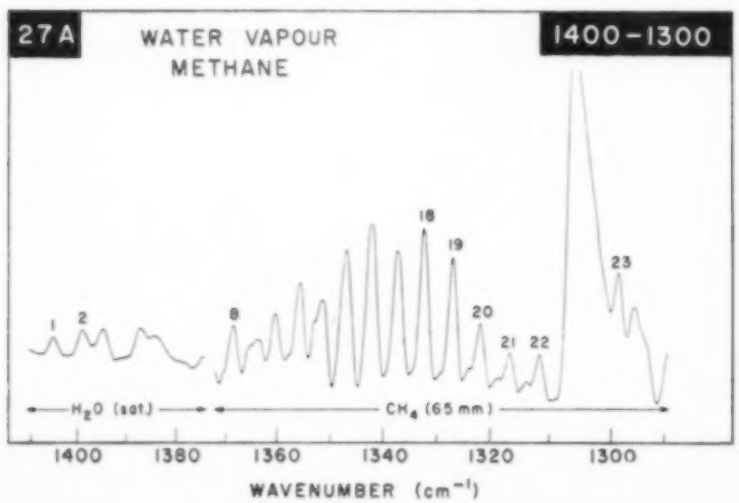

22 A
DEUTERIUM BROMIDE
WATER VAPOUR
1900 – 1800
1,2 3,4 5,6 7,8 9,10 11,12 13,14 15,16 19,20 21,22 23,24 25,26 27,28
DBr (60 mm)
29 31 32 36
H2O (sat.)
1900 1880 1860 1840 1820 1800
WAVENUMBER (cm⁻¹)

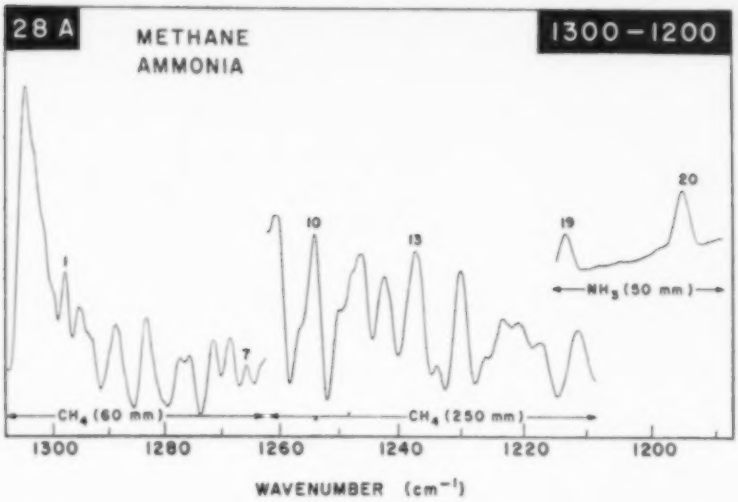

23 A
DEUTERIUM BROMIDE
WATER VAPOUR
1800 – 1700
1,2 3,4 5,6 7,8 9,10 11,12
DBr (60 mm)
21 23 26 27 29 33 37
H2O (sat.)
1800 1780 1760 1740 1720 1700
WAVENUMBER (cm⁻¹)

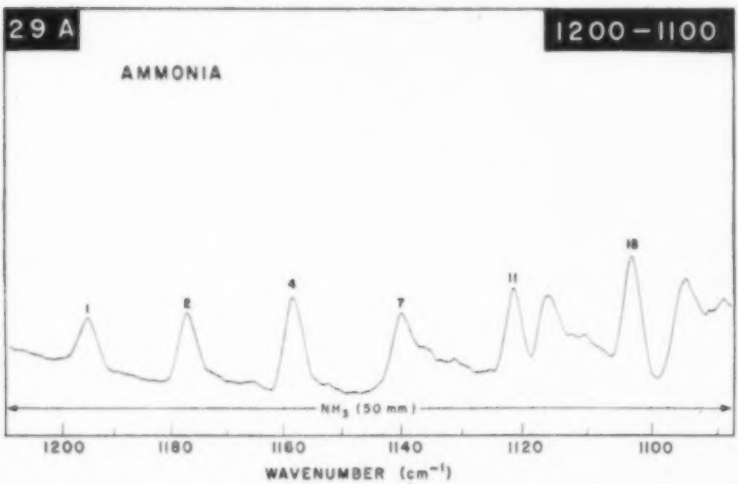

24 A
AMMONIA
WATER VAPOUR
1700 – 1600
3 5 6 7 11 13 17
NH3 (75 mm)
H2O (sat.)
1700 1680 1660 1640 1620 1600
WAVENUMBER (cm⁻¹)

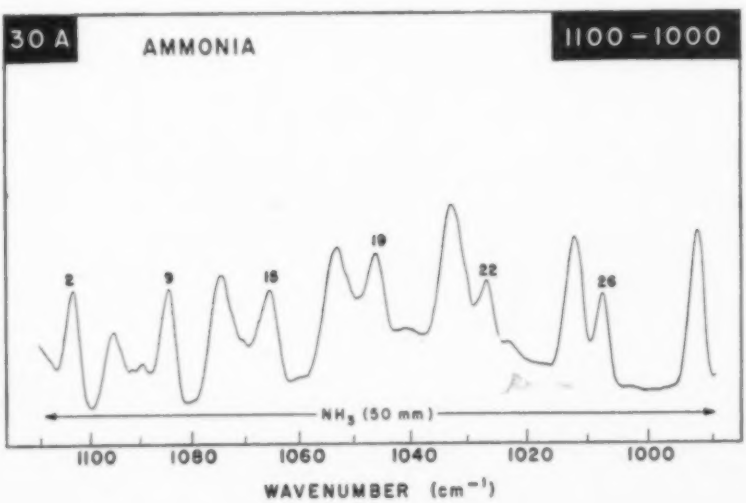

25 A
AMMONIA
WATER VAPOUR
1600 – 1500
5
6
8
11
16
24
NH3 (75 mm)
H2O (sat.)
1600
1580
1560
1540
1520
1500
WAVENUMBER (cm-1)

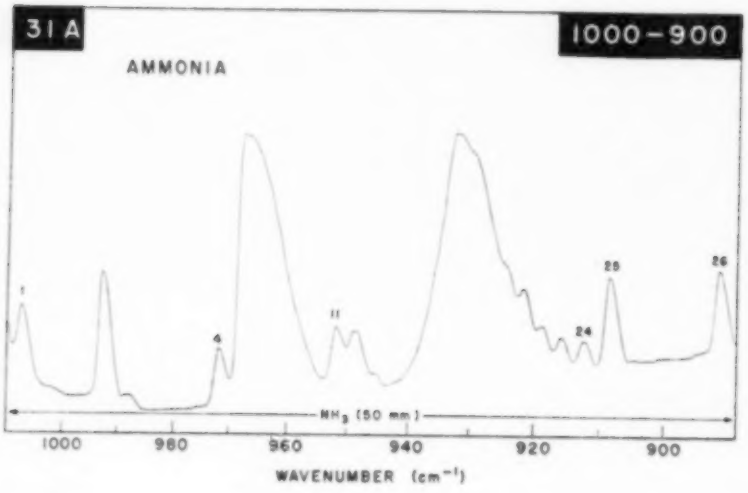

26 A
WATER VAPOUR
1500 – 1400
5
11
14
15
16
17
18
20
21
H2O (sat.)
1500
1480
1460
1440
1420
1400
WAVENUMBER (cm-1)

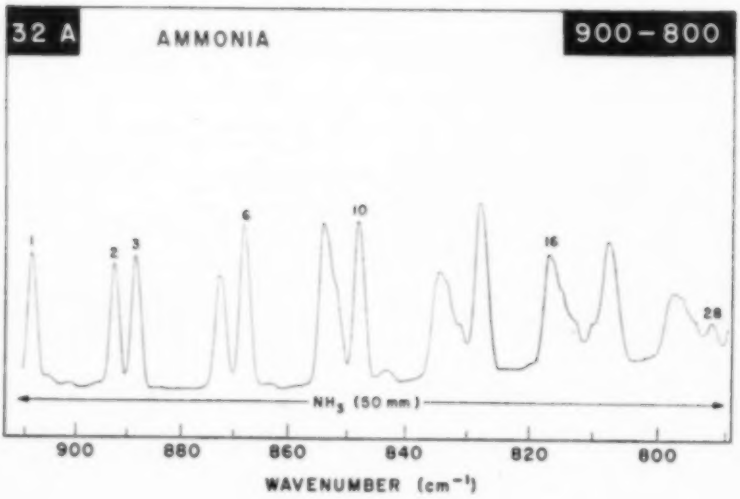

27 A
WATER VAPOUR
METHANE
1400 – 1300
1
2
8
18
19
20
21
22
23
H2O (sat.)
CH4 (65 mm)
1400
1380
1360
1340
1320
1300
WAVENUMBER (cm-1)


28 A
METHANE
AMMONIA
1300 – 1200
1
7
10
13
19
20
NH3 (50 mm)
CH4 (60 mm)
CH4 (250 mm)
1300
1280
1260
1240
1220
1200
WAVENUMBER (cm⁻¹)

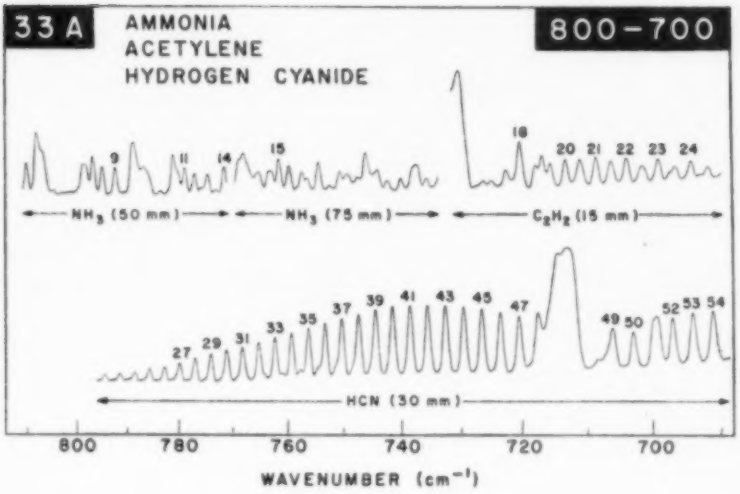

29 A
AMMONIA
1200 – 1100
1
2
4
7
11
18
NH3 (50 mm)
1200
1180
1160
1140
1120
1100
WAVENUMBER (cm⁻¹)

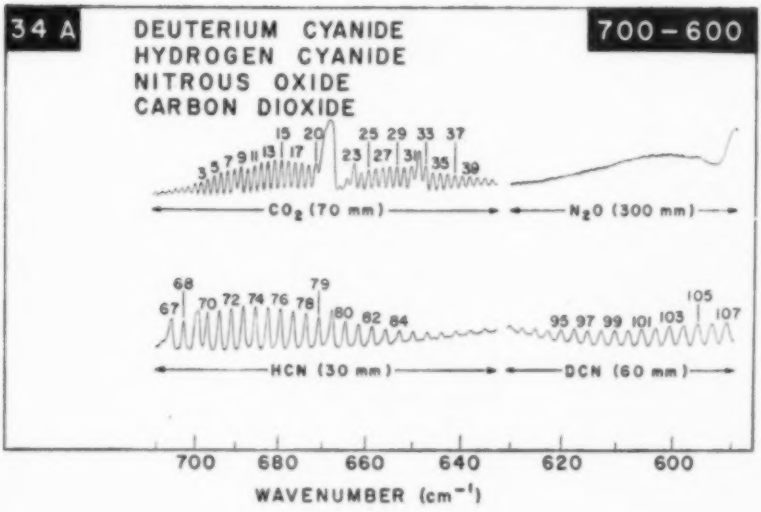

30 A
AMMONIA
1100 – 1000
2
9
15
19
22
26
NH3 (50 mm)
1100
1080
1060
1040
1020
1000
WAVENUMBER (cm⁻¹)


31 A
AMMONIA
1000–900
1
4
11
24
25
26
NH3 (50 mm)
1000
980
960
940
920
900
WAVENUMBER (cm⁻¹)


32 A
AMMONIA
900–800
1
2
3
6
10
16
28
NH3 (50 mm)
900
880
860
840
820
800
WAVENUMBER (cm⁻¹)

VOL.
1
1960


33 A
AMMONIA
ACETYLENE
HYDROGEN CYANIDE
800–700
9
11
14
15
18
20 21 22 23 24
NH3 (50 mm)
NH3 (75 mm)
C2H2 (15 mm)
27 29 31 33 35 37 39 41 43 45 47
49 50 52 53 54
HCN (30 mm)
800 780 760 740 720 700
WAVENUMBER (cm⁻¹)


34 A
DEUTERIUM CYANIDE
HYDROGEN CYANIDE
NITROUS OXIDE
CARBON DIOXIDE
700–600
3 5 7 9 11 13 15 17 20
23 25 27 29 31 33 35 37 39
CO2 (70 mm)
N2O (300 mm)
67 68 70 72 74 76 78 79 80 82 84
95 97 99 101 103 105 107
HCN (30 mm)
DCN (60 mm)
700 680 660 640 620 600
WAVENUMBER (cm⁻¹)